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FINAL REPORT

PART I

OZONE CHEMILUMINESCENT STUDY

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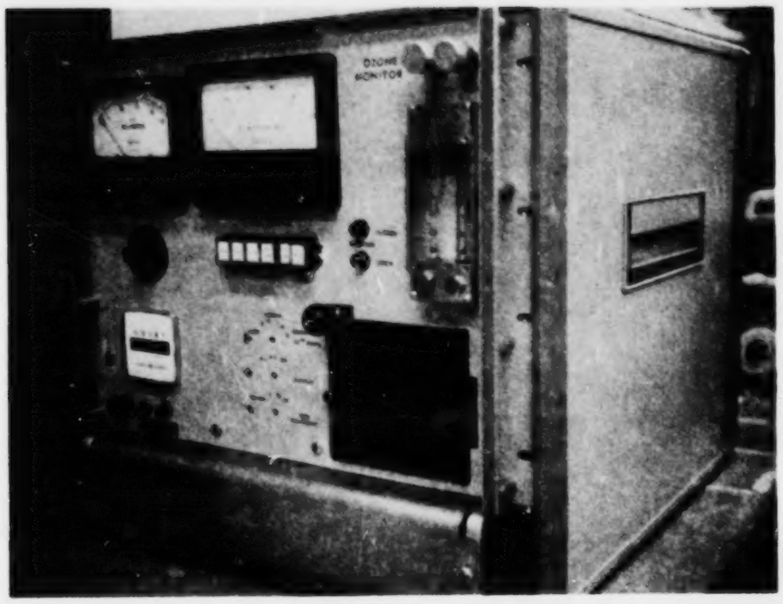
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

CHEMILUMINESCENT OZONE METER

Model EU-414



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FOREWORD

This report describes the results of a program to design, fabricate and test a feasibility model of a chemiluminescent ozone meter. The work has been administered by the Methods Development Branch, Chemistry and Physics Division, Bureau of Engineering and Physical Sciences, National Air Pollution Control Administration, Mr. Andrew E. O'Keeffe, Contract Officer.

This is Part I of two parts of the Final Report. Part II deals with the ozone generator phase of the contract. A prototype instrument and five additional models of the chemiluminescent ozone meter were delivered under this contract. Detailed operating and maintenance manuals were delivered with the instruments. In addition, several sets of working drawings, satisfactory for fabrication of the non-standard assemblies and compounds, were provided.

The program was conducted in the Engineering and Environmental Sciences Division of the Research Triangle Institute. Participating staff members and their principal area of contribution to the program and to this report are as follows:

H. G. Richter - chemiluminescent sensor
R. B. Strong - calibration procedures (excluding amplifier)
A. H. Truckner - mechanical design, and fabrication and test
J. H. White - amplifier design and testing
S. R. Stilley - amplifier fabrication, unit wiring and decal work
C. E. Moore - general chassis fabrication
D. R. Whitaker - detector design
C. E. Decker - instrument performance characteristics

Other members of the RTI staff whose critiques were a valuable aid in the program were J. R. Smith, J. J. B. Worth and Dr. R. M. Burger. In addition, we wish to acknowledge the valuable contributions of members of NAPCA, in particular, R. S. Stevens, Dr. J. Hodgeson, A. E. O'Keeffe throughout the course of the program.

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1.0 INTRODUCTION

The Research Triangle Institute has, under this phase of PHS Contract No. CPA 22-69-7 with the National Air Pollution Control Administration, conducted a program to design, fabricate and test an experimental ozone meter. Approximately midway through the program the contract was extended to include the fabrication and testing of five additional units.

The initial unit was considered a prototype unit and as such differs in some minor details from the five subsequent units. The latter models were as nearly identical in construction as practical. There are no basic differences in the operational characteristics of the instruments. Individual calibration curves for each unit; i.e., for the internal calibration assembly, for ozone concentration versus aperture setting and flow rate were included in the front of each manual.

This report is, in general, a comprehensive engineering description of the design, construction details, calibration techniques and operational characteristics of the ozone meter. The essential material in the instruction manual has been expanded, particularly with respect to the design, testing, and operational characteristics.

A complete set of drawings covering the non-standard components such as the detector assembly and calibration unit are available from the project officer.

The ozone meters utilize a chemiluminescent disc as the basic sensor. When ozone reacts with certain organic compounds, a minute amount of light is emitted; this light is collected and amplified by a photomultiplier tube. The electrical signal from the PM tube is then a function of the concentration of ozone passing over the chemiluminescent sensor.

A description of the chemiluminescent sensor is given in Section 2.0; the operational characteristics of the instrument are detailed in Section 3.0; and a detailed description of the design and test results for the various sub-assemblies are presented in Section 4.0. Various details concerning parts list, installation and maintenance of the instrument, calibration procedures, and operation procedures are included in the respective appendices.

2.0 CHEMILUMINESCENT SENSOR

2.1 Background

Most of the instruments currently in use for routine monitoring of trace oxidant concentrations are based on either coulometric or colorimetric techniques. In these methods iodide ions are oxidized to iodine by the oxidant when the gas being sampled passes over or through the solution. The electrical energy required to reduce this liberated iodine back to the iodide state is a measure of the oxidant concentration in coulometric instruments. In colorimetric instruments a ratio colorimeter is used to measure the color of the liberated iodine against a reference. Because of kinetic factors, however, not all oxidizing agents in the gas produce stoichiometric amounts of iodine. Compounds such as nitrogen dioxide do produce an instrument response. The contribution of other oxidizing agents in the atmosphere to the "total oxidant" meter reading is usually not known. Reducing agents in the atmosphere, such as sulfur dioxide, have the opposite effect. Various types of "scrubbers" such as paper strips saturated with CrO_3 or chromic acid solution are used to eliminate the interference from SO_2. Experience has shown that the technique is not completely satisfactory.[1]

The chemiluminescent technique of Bernanose and Réné[2] and Regener[3] on the other hand is specific for ozone. In order for interferences to occur, extremely high concentrations of the usual interfering substances are required. The principle of operation takes advantage of the fact that certain organic compounds emit small quantities of light when they react with ozone. Luminol was used first by Bernanose and Réné[2] and Regener.[4] Regener also found that Rhodamine-B yielded more reproducible results than did luminol.

The Rhodamine-B is adsorbed on the surface of silica-gel and then deposited on an aluminum disc.[5] Gases to be sampled are passed over the disc and the emission of light resulting from the reaction with ozone is measured using a photomultiplier tube. Various interference tests using compounds normally found in a polluted atmosphere. for example, have indicated a negligible effect upon the response characteristics of the disc.[6]

As originally built, the first ozone-sensors suffered serious interference from atmospheric moisture. Provisions were incorporated in the early instruments to minimize this effect. The fundamental reason for building this new instrument was the development of sensors which were insensitive to moisture. Use of these permitted simplification of the instrument. In addition, improved electronic components and circuitry permitted construction of an instrument which could take advantage of the new sensor's properties.

2.2 Chemiluminescent Disc Preparation

The ozone-sensors are 2-inch diameter discs of finely divided silica-gel deposited with a binder on a photographic film support (Eastman Kodak "Chromagram" sheets). In the present technique of preparing the sensors, discs of the Chromagram are dehydrated at 110°C for an hour, then immediately dipped for one minute in a 10 percent (w/w) solution of a silicone resin (General Electric Co. type SR-82). The coated discs are again dried at 110°C for 18-24 hours, then dipped for 1 minute in a 0.1 percent solution of Rhodamine-B in acetone. Discs so prepared, if protected from extended exposure to bright light, are stable for several months and need not be stored in a dry atmosphere.

2.3 Disc Activation

Rhodamine-B discs prepared as above do not exhibit much sensitivity to ozone when first placed in the ozone meter. They must be "activated". A common technique is to expose the disc to ozone for some period of time. The phenomena occurring during this activation period are not understood. One plausible explanation is that ozone-reactive impurities are deposited on the surface together with the SR-82 or Rhodamine-B, which impurities must be removed or destroyed before the chemiluminescent reaction can be observed. Whatever the reason, the steady signal for a constant ozone concentration passing over the disc is attained only after 12-24 hours of "activation", the time being shorter for higher concentrations of ozone. Thereafter, the disc can be removed from the instrument for many days, then replaced, without having to repeat the activation process.

An activated disc is usable for long periods of time. The exact length is dependent upon the total amount of ozone which passed over it, and the minimum sensitivity which the user is willing to accept. Since the ozone-Rhodamine-B reaction results in destruction of the organic molecule, less and less of the compound remains as the disc is used. With enough experience and a series of discs prepared in identical manner, it might be possible to determine the usable life of a disc but such information is not available at the present time. The sensitivity of the disc will decrease as the Rhodamine-B is destroyed and will at some time fall to a value which will no longer be acceptable to the user. At this time the disc will be said to be exhausted and have to be replaced. Discs prepared, as described above, have lifetimes of two or three weeks when exposed continuously to 30 pphm of ozone. This is a rigorous usage and in normal monitoring operations the disc will last much longer.

2.4 Disc Characteristics

It is possible to prepare Rhodamine-B discs which have, after activation, an initial sensitivity such that one can easily measure ozone concentrations of less than 1 ppb. As the Rhodamine-B is consumed, however, the sensitivity decreases.

It has been found that some discs are also slightly sensitive to humidity. In one series of tests, for example, equal volumes of dry air and ozonized air were mixed, sampled, and yielded a normalized signal of 1.0. When water saturated air was substituted for the dry air and mixed with equal volume of ozonized air (50 percent RH), the signal increased to a normalized value of 1.13. The dry, ozonized sample again yielded a normalized signal of 1.0 within five minutes after the moisture was removed. The observation is repeatable at higher and lower ozone concentrations. At 73 percent RH the normalized signal increased from 1.0 to 1.19.

This moisture sensitivity may or may not be of serious concern. It should be possible to prepare discs which are moisture insensitive. Even with the present discs, however, if ambient humidity varies from 50 percent to 100 percent, the error in instrument readings should not be greater than ± 10 percent.

If after initial activation, the disc is exposed to relatively high concentration of ozone until a steady signal is obtained, and then suddenly the ozone source is removed, the signal drops rapidly during the first minute or so after source removal and then decreases slowly in almost a power-law relation over the next few hours. The time required to reach the original zero ozone signal level, from the high current level, is dependent both on the magnitude of the current and how long the disc has been exposed to that ozone concentration.

Conversely, if the disc has been exposed to no ozone for a period of time and then suddenly subjected to a relatively high concentration, such as is done in calibrating the disc periodically, either of two phenomena may be observed: either there is an initial, rapid signal increase--a "spike"--followed by slow decrease to steady signal, or there is a slow rise to steady signal--no spike. The presence or absence of the spike is dependent on disc characteristics, but the preparative procedure for producing either of these reactions at will is not known. At any rate, the time required to reach a steady signal is dependent on the length of time during which the disc has remained unexposed to ozone.

These characteristics of the sensor disc are related to the use of Rhodamine-B. Several different preparative procedures all yield similar results. Because they do influence response-times between steady-state signals, these disc characteristics restrict usage of the instrument to those situations where rapidly changing ozone concentrations are not encountered, or are unimportant.

2.5 Summary

Rhodamine-B discs as presently prepared must be activated before they chemiluminesce when acted upon by ozone. Thereafter, they are sensitive to ozone concentrations as low as 1 ppb for an extended period of time. Some disc preparations also are slightly sensitive to humidity. Since Rhodamine-B is decomposed by ozone, the discs slowly decrease in sensitivity until they no longer yield enough light for the experiment.

Rhodamine-B discs sometimes exhibit long time-response characteristics, depending on the method of disc preparation. For example, several hours may elapse before the emitted light has decreased to an insignificant value after a particularly high ozone concentration has been sampled for a long time. Also, after some activated discs have been exposed to clean air for an extended period, they may require up to an hour to achieve a steady signal from a constant ozone source.

For an instrument in which rapid time-response is not important and in which a standard calibration source can be routinely sampled, Rhodamine-B discs as presently prepared are satisfactory.

3.0 OZONE METER FUNCTIONAL AND OPERATIONAL CHARACTERISTICS

3.1 Theory of Operation

The principle on which the chemiluminescent ozone meter operates is as follows: when ozone reacts with certain organic compounds, a minute amount of light is emitted. The amount of light is directly proportional to the ozone concentration, and the wavelength of the emitted light is a function of the organic compound or dye used in the formation of the chemiluminescent disc. Gases to be sampled are passed over a disc coated with the dye. The emitted light resulting from the reaction with ozone is detected by means of a sensitive photo-detector.

3.2 Functional Description

A functional diagram of the proposed ozone meter is shown in Fig. 1. The basic element of the system is the chemiluminescent disc and photo-detector assembly. The gases to be sampled are metered at a constant flow rate across the disc. The emitted light resulting from the reaction of ozone with the chemiluminescent material is monitored by the photomultiplier tube.

The system has essentially two modes of operation. During the RUN mode gases are pulled through the test-air inlet, mixed with the dilution flow, and then passed over the disc. During the CALIBRATE mode the sample-gas inlet is closed and the calibrate line is opened by means of electrically actuated solenoid valves. Air which enters the calibrate inlet passes through a drying tower which removes contaminants, particularly water vapor, and destroys any ozone present.

A controlled amount of ozone is generated in the "clean air" as it passes through the calibration unit by exposing the air stream to an ultra-violet light source. A calibrated aperture control facilitates varying the ozone concentration. A front panel control and meter provides for lamp current control and monitoring, respectively.

The gases are metered at a constant flow rate of 600 ml/min through the disc chamber. The inlet gas is regulated at 100 ml/min and mixed with the 500 ml/min dilution flow. Flow meters and vernier control valves are located on the front panel of the instrument. The timing and control unit provides the necessary switching voltages for actuating the various solenoids. Selection of operating modes is made by means of front-panel push-button switches.

The light emission from the disc is detected by means of a sensitive photomultiplier tube. The output of the PM tube is amplified and presented on a panel meter and at a recorder output connector. Five linear-decade current ranges and one three-decade logarithmic range is provided. In addition, a X1, X½, and X¼ output attenuator is provided for scale adjustment. An AC-integrator or time-constant control is incorporated in the amplifier which facilitates smoothing of the analog data. A manually operated shutter incorporated in the disc chamber allows for monitoring of the PM tube dark current. High voltage for the PM tube is provided by a well regulated, adjustable HV supply.

The output signal to dark current ratio for a given concentration of ozone is a direct function of the sensitivity of the disc and the quantum efficiency of the photomultiplier tube in the spectral region of the emitted light. Since the dark current and the quantum efficiency vary considerably from tube to tube one may expect a factor of 10 or more in this ratio. With tube selection this may be reduced to a 10-20% variation from unit to unit.

The system design includes selectable modes which insert a calibrate signal, for some preselected length of time, every 6 or 12 hours and a sampling-cycle mode which consists of a 1 min-measure, 1 min-purge, 1 min-calibrate, and 1 min-purge cycle. In addition, push-button actuated modes are available for operating continuously in the RUN or CALIBRATE modes; these facilitate test and calibration procedures. An EXTERNAL mode is provided for remotely controlling the operational mode of the instrument.

3.3 Physical Description

A front panel view of the ozone meter illustrating the type and location of all controls, meters, etc., is shown in Fig. 2. The cover for the HV supply, which is normally in place, is shown removed for purposes of illustration.

There are two basic units, the main chassis and the HV power supply. The latter is located in the bottom of the cabinet. The main chassis is mounted on chassis slides and may be readily pulled out on the chassis slides for adjustment and testing purposes. A rear view of the instrument is shown in Fig. 3. A plan view of the main chassis is given in Fig. 4, showing the relative positioning of the major components and assemblies.

Both the main chassis and HV power supply fit into the standard 19" width cabinet. The overall physical dimensions of the instrument are as follows:

Height - 18.5 inches,
Width - 19.75 inches,
Depth - 23 inches,
Weight - 133 lbs.

The unit requires approximately 290 watts of power from a 115V, 60 Hz single phase source. A block diagram illustrating the AC and DC power distribution is given in Fig. 5.

3.4 Instrument Specifications

SYSTEM:

Dynamic Range - 1 pphm to 10 ppm
Resolution - 0.1 pphm
Minimum Detectable Level - 1 pphm
Precision - 2%
Accuracy - ± 10% at time of calibration
Stability - primarily dependent on disc characteristics and sample air composition
Calibration - nominal range 20 - 30 pphm
internally adjustable 0 - 20 pphm
Output - front panel meter 0 - 10 units
recorder output - 1 volt FS; max rated output - 5 mA

AMPLIFIER:

Output Meter - full scale value indicated by SENSITIVITY and FS OUTPUT control settings
Sensitivity - log - 10^{-9} to 10^{-6} amps
linear - 10^{-9} amps, FS
10^{-8} " "
10^{-7} " "
10^{-6} " "
10^{-5} " "
Stability - log - < 0.5% for 60 hrs (for worst case condition)
linear - 0.01% per°C; 1% per month (for 10^{-9} amp range)

3.5 Front Panel Controls and Indicators

MODE CONTROLS:

Ext. - external timing control
Cal. Cont. - continuous CALIBRATE
Run. Cont. - continuous RUN
12 hr - continuous RUN, calibration once every twelve hours
6 hr - continuous RUN, calibration once every six hours
Samp. - four minute cycle: one minute measure, one minute purge, one minute calibrate, one minute purge

AMPLIFIER:

FS Output - modifies full scale sensitivity by factor of 1, ½ or ¼
Time Constant - normal, 1 sec, 10 sec, 40 sec
Offset - provides dark current offset control from 0 - 10^{-8} amps

LAMP CURRENT - controls calibration lamp current

ELAPSED TIME METER - hours and 1/10 hours, actuated during power ON condition

AC POWER - single switch turns entire system ON

FLOW CONTROL - valves and flowmeters for dilution and total flow control and monitoring

SHUTTER - open for operation; close for dark current check and disc removal/replacement

DISC ACCESS DOOR - allows removal/replacement of disc

INTERLOCK SYSTEM - indicates shutter control status; warning buzzer when disc access door opened without fully closing shutter

HV POWER SUPPLY:

Power Switch - ON position
HV Controls - normally set for value which yield PM tube gain = 200
Cover - normally left in place

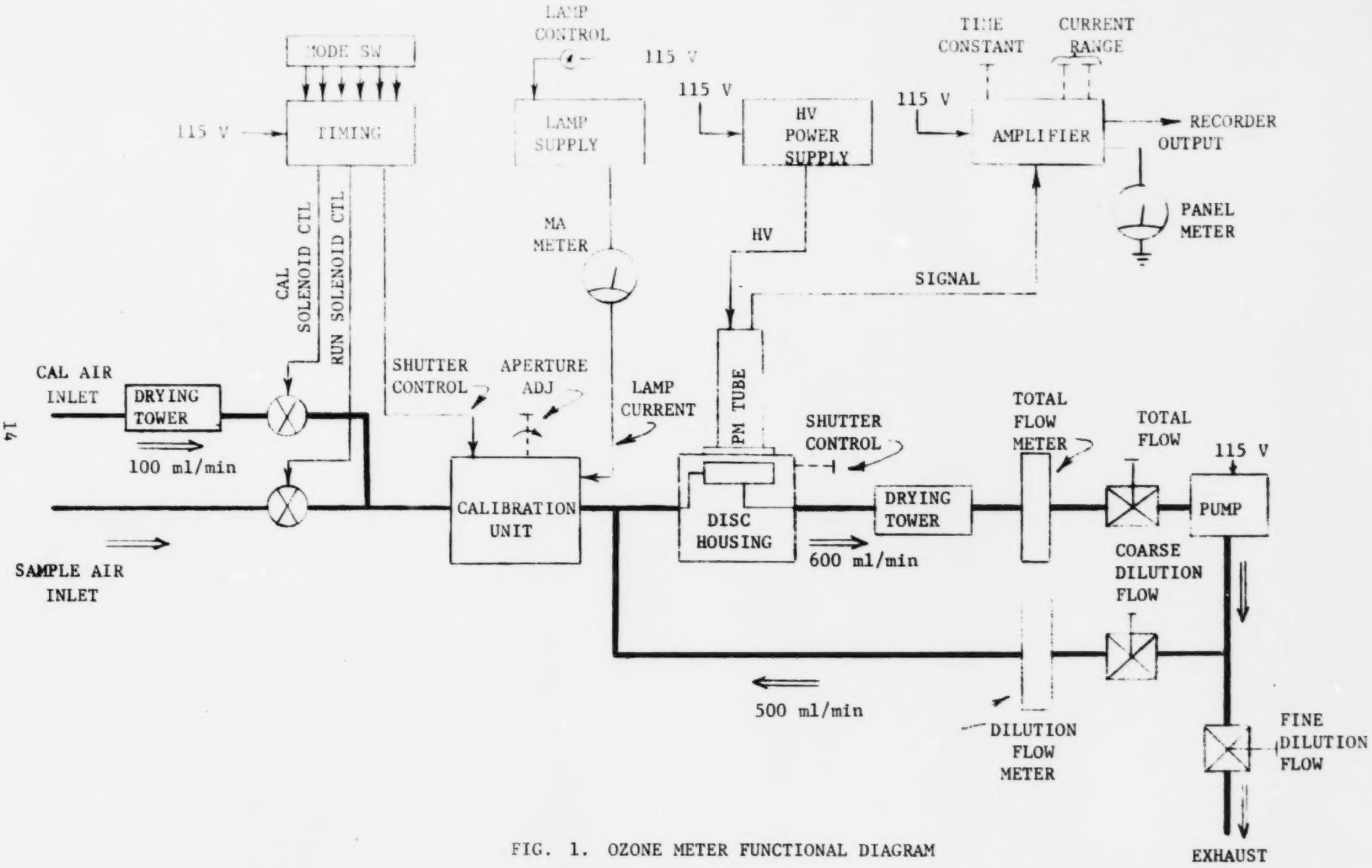

MODE SW
115 V
TIMING
CAL SOLENOID CTL
RUN SOLENOID CTL
LAMP CONTROL
115 V
LAMP SUPPLY
MA METER
115 V
HV POWER SUPPLY
HV
TIME CONSTANT
CURRENT RANGE
115 V
AMPLIFIER
RECORDER OUTPUT
PANEL METER
SIGNAL
CAL AIR INLET
DRYING TOWER
100 ml/min
SAMPLE AIR INLET
SHUTTER CONTROL
APERTURE ADJ
LAMP CURRENT
CALIBRATION UNIT
PM TUBE
SHUTTER CONTROL
DISC HOUSING
600 ml/min
DRYING TOWER
TOTAL FLOW METER
TOTAL FLOW
115 V
PUMP
COARSE DILUTION FLOW
500 ml/min
DILUTION FLOW METER
FINE DILUTION FLOW
EXHAUST

FIG. 1. OZONE METER FUNCTIONAL DIAGRAM

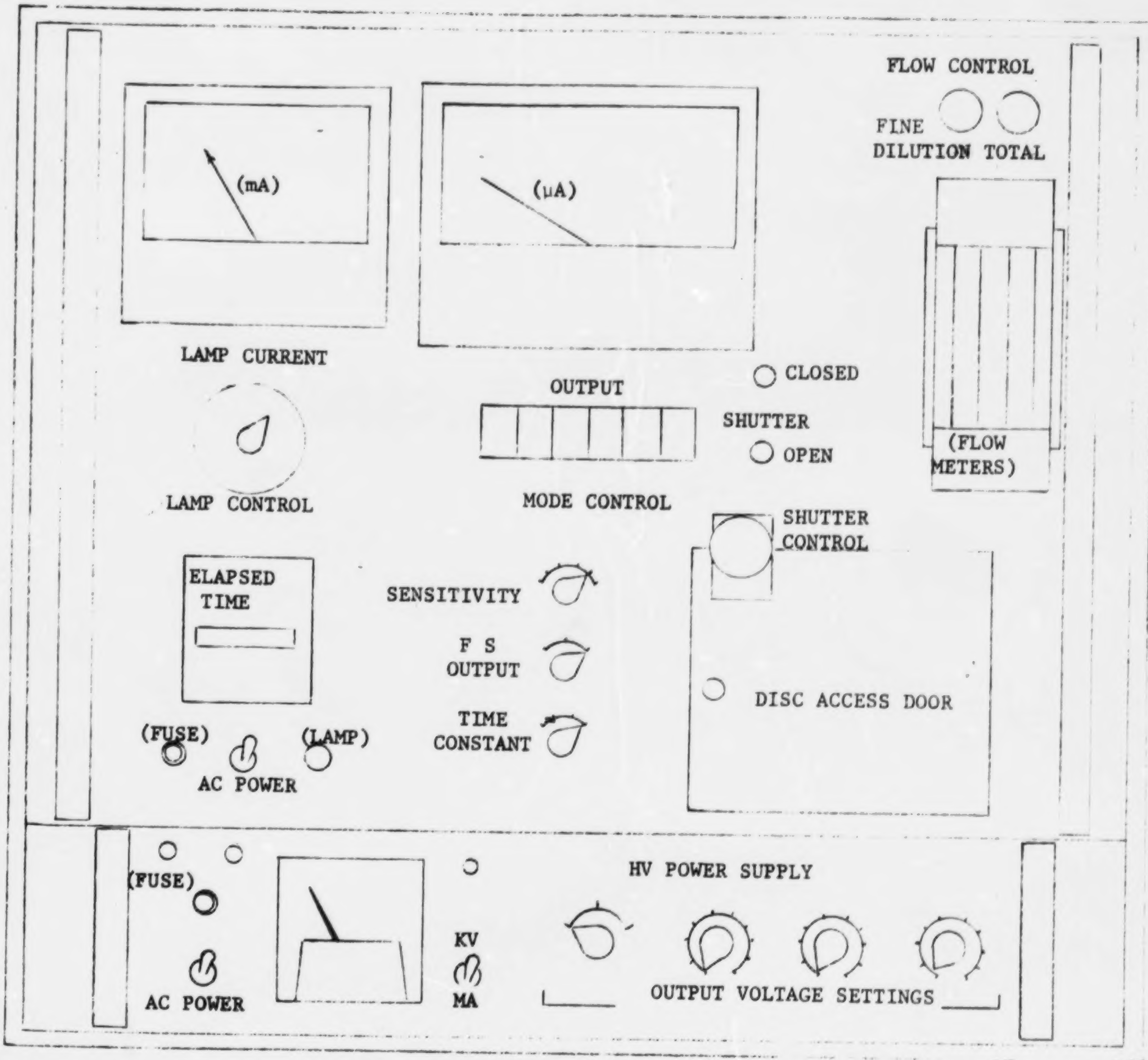

FLOW CONTROL
FINE
DILUTION TOTAL
(mA)
(μA)
(FLOW METERS)
LAMP CURRENT
LAMP CONTROL
OUTPUT
MODE CONTROL
CLOSED
SHUTTER
OPEN
SHUTTER CONTROL
ELAPSED TIME
SENSITIVITY
F S OUTPUT
TIME CONSTANT
DISC ACCESS DOOR
(FUSE)
(LAMP)
AC POWER
(FUSE)
AC POWER
KV
MA
HV POWER SUPPLY
OUTPUT VOLTAGE SETTINGS

FIGURE 2. FRONT PANEL VIEW OF OZONE METER (with HV power supply cover removed)

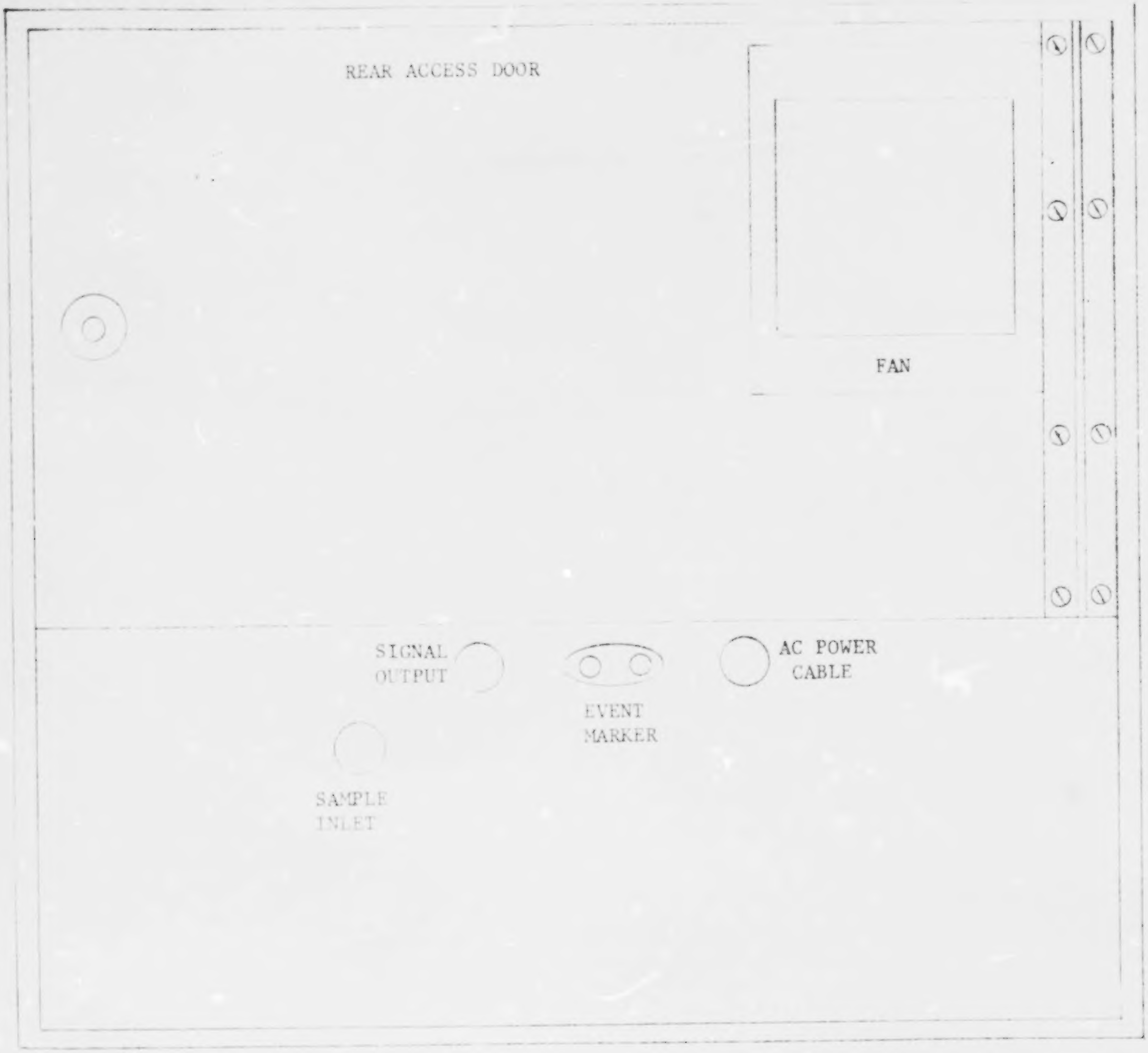

REAR ACCESS DOOR
FAN
SIGNAL OUTPUT
EVENT MARKER
AC POWER CABLE
SAMPLE INLET

FIGURE 3. REAR PANEL VIEW OF OZONE METER

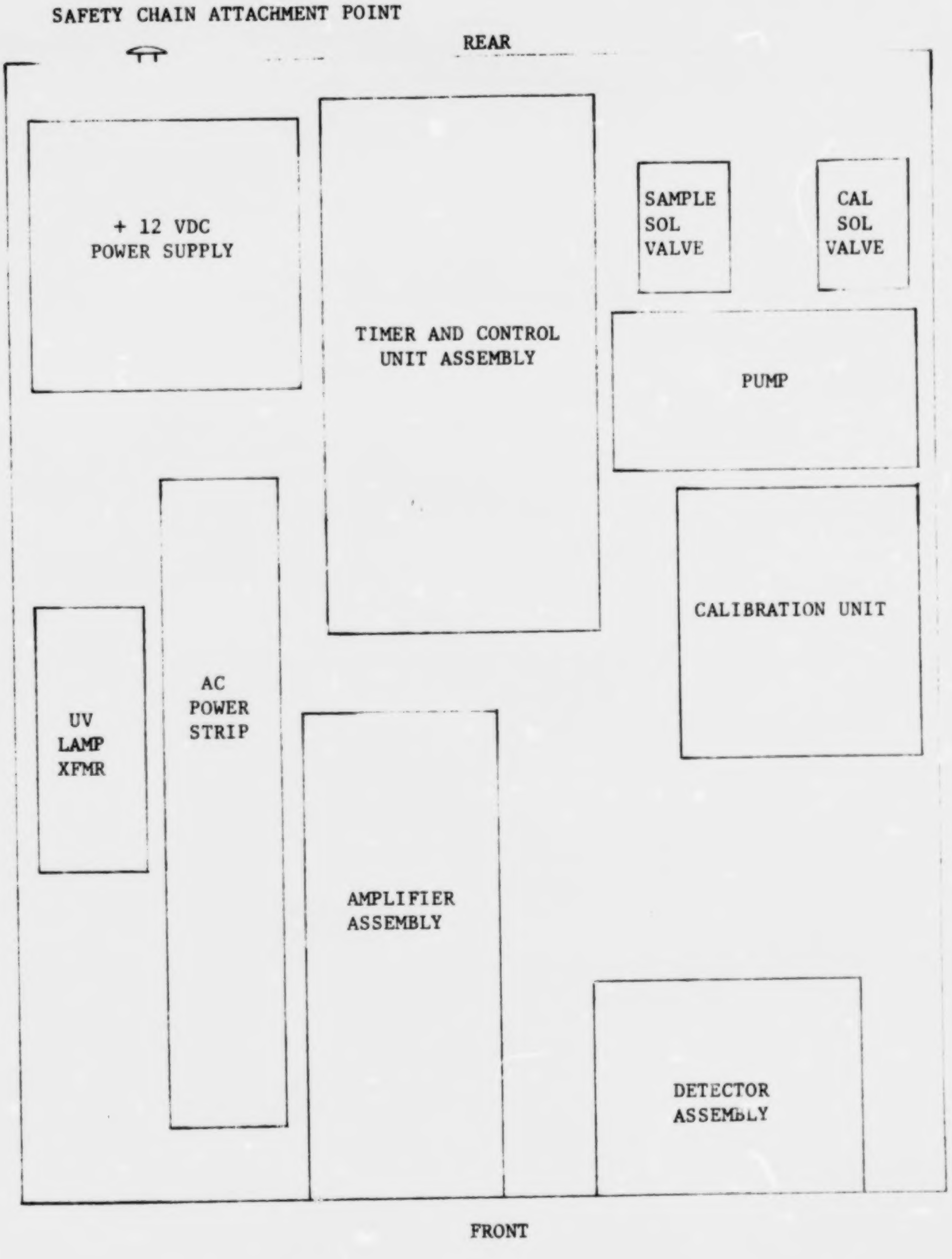

SAFETY CHAIN ATTACHMENT POINT
REAR
+ 12 VDC
POWER SUPPLY
TIMER AND CONTROL
UNIT ASSEMBLY
SAMPLE
SOL
VALVE
CAL
SOL
VALVE
PUMP
CALIBRATION UNIT
UV
LAMP
XFMR
AC
POWER
STRIP
AMPLIFIER
ASSEMBLY
DETECTOR
ASSEMBLY
FRONT

FIGURE 4. MAIN CHASSIS LAYOUT

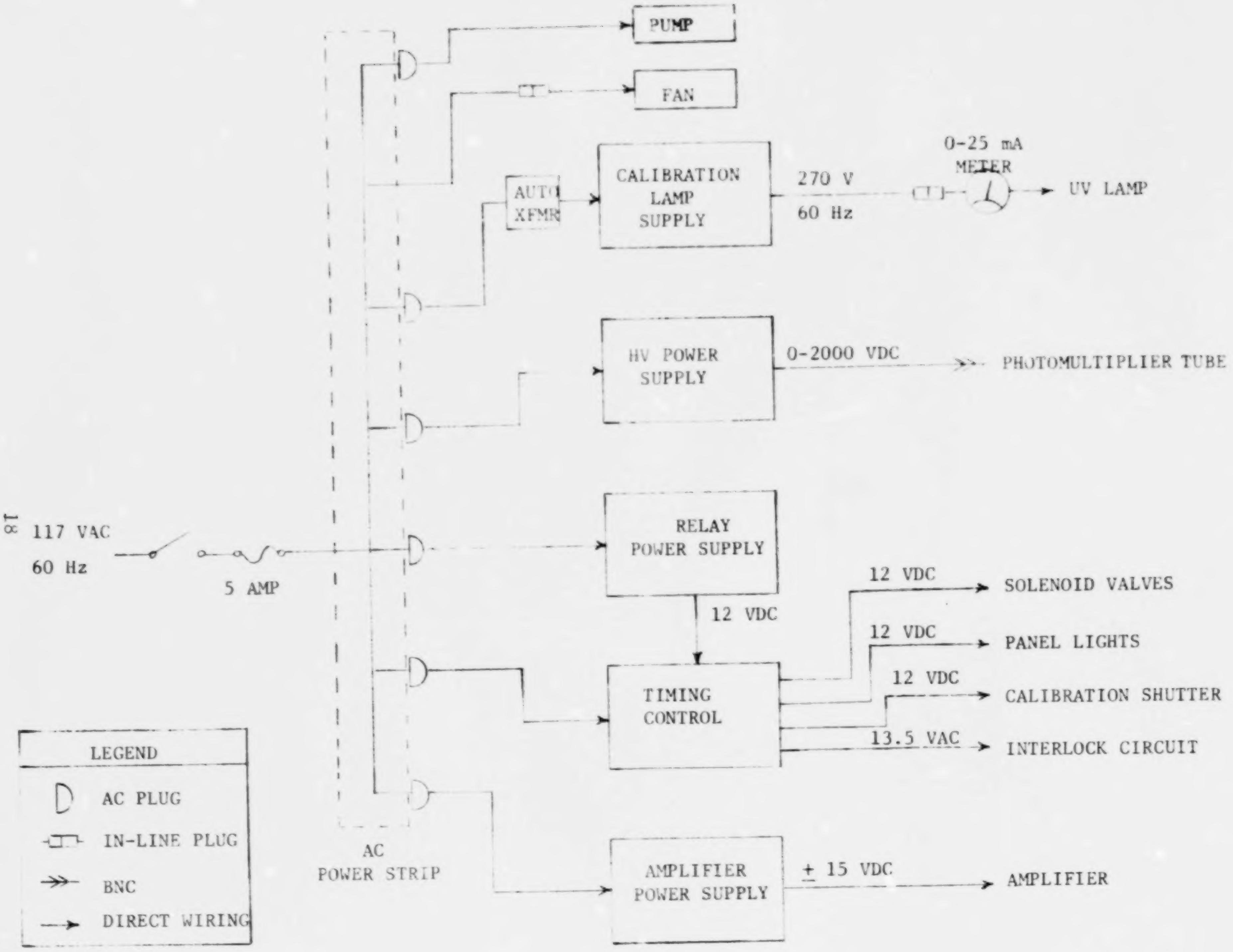

PUMP
FAN
AUTO XFMR
CALIBRATION LAMP SUPPLY
270 V
60 Hz
0-25 mA METER
UV LAMP
HV POWER SUPPLY
0-2000 VDC
PHOTOMULTIPLIER TUBE
117 VAC
60 Hz
5 AMP
RELAY POWER SUPPLY
12 VDC
TIMING CONTROL
12 VDC
SOLENOID VALVES
12 VDC
PANEL LIGHTS
12 VDC
CALIBRATION SHUTTER
13.5 VAC
INTERLOCK CIRCUIT
AC POWER STRIP
AMPLIFIER POWER SUPPLY
± 15 VDC
AMPLIFIER
LEGEND
AC PLUG
IN-LINE PLUG
BNC
DIRECT WIRING

FIGURE 5. AC AND DC POWER DISTRIBUTION

3.6 Performance Characteristics

The single most important set of specifications for the instrument is the performance characteristics. Some of these were tabulated in Section 3.4. A brief description of the more pertinent performance characteristics will be given in this section. Detailed descriptions and performance criteria are given in Section 4.0 for the respective sub-assemblies.

3.6.1 Lag, Response, and Decay Time -- Lag, response, and decay time of the chemiluminescent ozone meter was determined in both the calibrate and measure mode of operation and at four time constant positions of the amplifier. Lag time is defined as the time interval required for a readable change in recorded output following introduction of ozone to the system. Response time is the time interval required to reach 95 percent of the final recorded output following introduction of ozone to the system. Decay time is the time required to reach 95 percent of the base line or zero reference level after removal of the ozone source.

A known concentration of ozone (≈ 20 pphm) was produced using the UV calibration source to determine these three parameters in both the calibration and measure mode. In both cases the instrument output was recorded on a strip-chart recorder at a chart speed of 4 inches per minute. At this speed it was convenient to monitor the chart record at three second intervals. Lag and response time were determined simultaneously by measuring the time required for initial response and ultimate output following introduction of ozone at the instrument inlet for the measure mode and through the calibration unit in the calibrate mode.

Decay time was determined by closing the shutter of the calibration box and monitoring the time for decay of the signal to 95 percent of the ultimate disc current, which is defined as the level of signal output produced when air containing no ozone is allowed to flow over the disc. Results of the above tests are summarized in Table 1.

Table 1

LAG, RESPONSE, DECAY TIME (≈ 20 pphm ozone)

Mode of Operation	Amplifier Time Constant	Lag Time (sec)	Response Time (sec)	Decay Time (sec)
Calibrate	N	3	7	10.5
	1	4	8	22.5
	10	5	52	71.0
	40	9	520	50.1
Measure	N	6	14	15
	1	8	60	25
	10	12	130	108
	40	15	540	660

From inspection of the data and the plumbing system it may be seen that the bulk of the delay is due to the length of tubing between the O_3 source and the disc neglecting the time constant effect.

3.6.2 Sensitivity, Resolution, Dynamic Range -- The sensitivity of the instrument can be defined as the minimum detectable level of ozone concentration and is dependent on the sensitivity of the disc and the characteristics of the phototube. Data indicate that one can detect ozone concentrations on the order of 1 ppb ozone in ambient air using a freshly prepared Rhodamine-B disc as described in Section 2.2. A decrease in instrument sensitivity occurs as the Rhodamine-B on the disc is consumed.

The resolution of the instrument can be defined as the minimum ozone concentration change which produces a significant change in output signal. Using a freshly prepared disc the resolution of the instrument is on the order of 0.1 pphm. The resolution of the instrument is basically a function of the PM tube and input amplifier noise and sensitivity of the disc.

The dynamic range of the instrument is estimated to cover at least a range of 10^4 (i.e., 1 ppb - 10 ppm). This again depends on disc characteristics and the voltage or gain applied to the phototube. The amplifier is calibrated in 5 linear current ranges, from 10^{-9} amps FS to 10^{-5} amps FS. Assuming the disc response is linear, then the system may be adjusted for a dynamic range of 10^4, with the most sensitive range providing a precise reading of the PM tube dark current.

3.6.3 Stability and Repeatability -- The stability of the instrument cannot be divorced from the characteristics of the Rhodamine-B sensor. The stability of the various sub-assemblies, such as the calibration unit, photomultiplier-tube, power supply, amplifier, and inlet flow rate into the instrument is discussed in Section 4.0. In general, however, the stability of the instrument is primarily dependent on the chemiluminescent disc. Dark current is directly affected by the PM tube temperature and this can be a significant effect at very low concentrations of ozone.

The repeatability or precision of the instrument is again primarily a function of the characteristics of the disc. Repeatability of the measurement and calibrate signal should be quite good when monitoring ambient ozone levels using a "stable disc", where decrease in signal is a function only of consumption (decay) of the Rhodamine-B disc.

3.6.4 Moisture Effects -- It is interesting and important to note that the calibration signal is not affected by changes in relative humidity. In a series of experiments, dry air was passed over an external UV lamp, followed by air saturated with moisture at the same flow rate. No variation in signal could be detected. While this may seem in contradiction to the previous observations about moisture sensitivity of the disc, one possible explanation is that a decrease in ozone generation efficiency in moist air by the UV lamp was just counterbalanced by the increased signal from the moisture sensitive disc. This point will have to be investigated further with other discs.

The observations have significance, too, with respect to the state of the desiccant columns in the instrument. If discs can be prepared which have no moisture sensitivity, then the recirculation desiccant columns can be replaced by a small amount of charcoal or MnO_2, just to destroy the ozone in the bypass loop. The desiccant column in the calibration air line may be replaced by a similar charcoal column if it can be demonstrated that the magnitude of the resulting calibration signal is independent of ambient relative humidity.

3.6.5 Flow Rate Characteristics -- An experiment was conducted to simulate effects of pressure and inlet flow rate variations when the instrument is operated from a manifold common to other air monitoring equipment. Variation in inlet flow rate under normal operating conditions was determined to be less than 2 percent during a 24 hour period. This was determined by monitoring the inlet flow with a Hasting mass flowmeter with the total and dilution rotameter set at the appropriate values and undisturbed for this period.

A. Calibration Mode

The effect of variation in inlet flow rate on instrument response in the calibration mode of operation was determined using the set-up in Fig. 6. Air flow rate into the instrument was varied from 50 to 215 ml/min by adjusting a micrometer valve and monitored using the Hastings mass flowmeter. Instrument output was recorded on a HP-680 strip chart recorder and inlet pressure determined with a water manometer. Results of these tests are included in Table 2.

Table 2

EFFECT OF INLET FLOW RATE VARIATION ON INSTRUMENT IN CALIBRATION MODE

Flow Rate (ml/min)	ΔP (in H_2O)	Signal Output (% Chart)
50	-7.2	51.0
68	-6.5	51.0
96	-1.3	51.5
100	-0.3	52.0
125	-0.3	52.0
140	-0.3	52.0
160	-0.3	52.0
187	-0.3	52.5
215	-0.3	52.5

From Table 2 it can be seen that changes in flow rate through the calibration box over the range (50 to 215 ml/min) affected the output signal by less than 2 percent. Although the concentration of ozone generated is proportional to the flow rate through the calibration box (see Section 4.4), the net concentration of ozone presented to the sensor

(Rhodamine-B disc) remains constant due to increased or decreased dilution ratio.

B. Measure Mode

Figure 7 is a diagram of the set-up used to determine the effect of variation of inlet flow rate in the measure mode. Measurement techniques for the various parameters (air flow rate, ΔP, signal output) were the same as presented in part A. Inlet flow rate was varied from 50 to 150 ml/min. Results of these tests are included in Table 3.

From Table 3 it is apparent that changes in inlet flow rate seriously affects signal output in the measure mode. A linear relationship (see Fig. 8) exists between flow rate and signal output (i.e., a decrease of 50 percent in signal output is seen when flow rate is decreased 50 percent). Serious measurement errors will occur in the measurement mode, unless the inlet flow rate is maintained exactly at 100 ml/min.

Table 3

EFFECT OF INLET FLOW RATE VARIATION ON INSTRUMENT OUTPUT IN MEASURE MODE

Flow Rate (ml/min)	ΔP (in H_2O)	Signal Output (% Chart)
50	-7.2	26
60	-6.9	31
70	-6.5	36
80	-3.6	40
90	-2.3	46
100	-0.3	52
120	-0.3	59
150	-0.3	70
200	-0.3	84

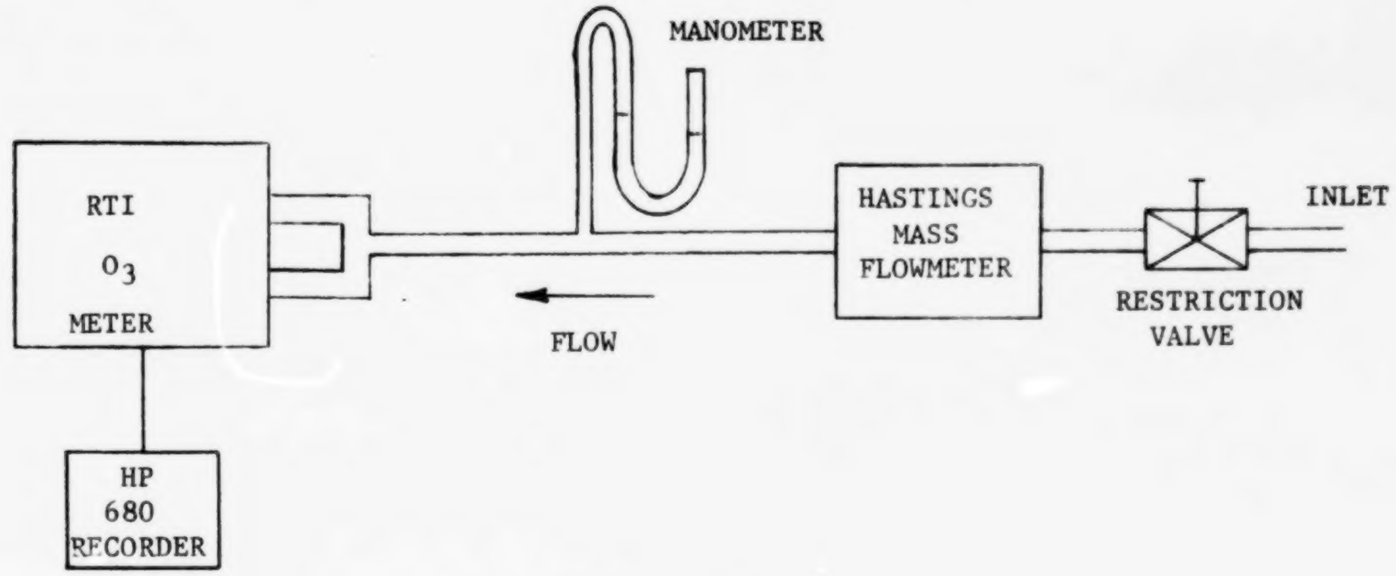

MANOMETER
RTI
O_3
METER
HASTINGS
MASS
FLOWMETER
INLET
RESTRICTION
VALVE
FLOW
HP
680
RECORDER

FIGURE 6. TEST SET-UP FOR CALIBRATION MODE FLOW-RATE CHARACTERISTICS

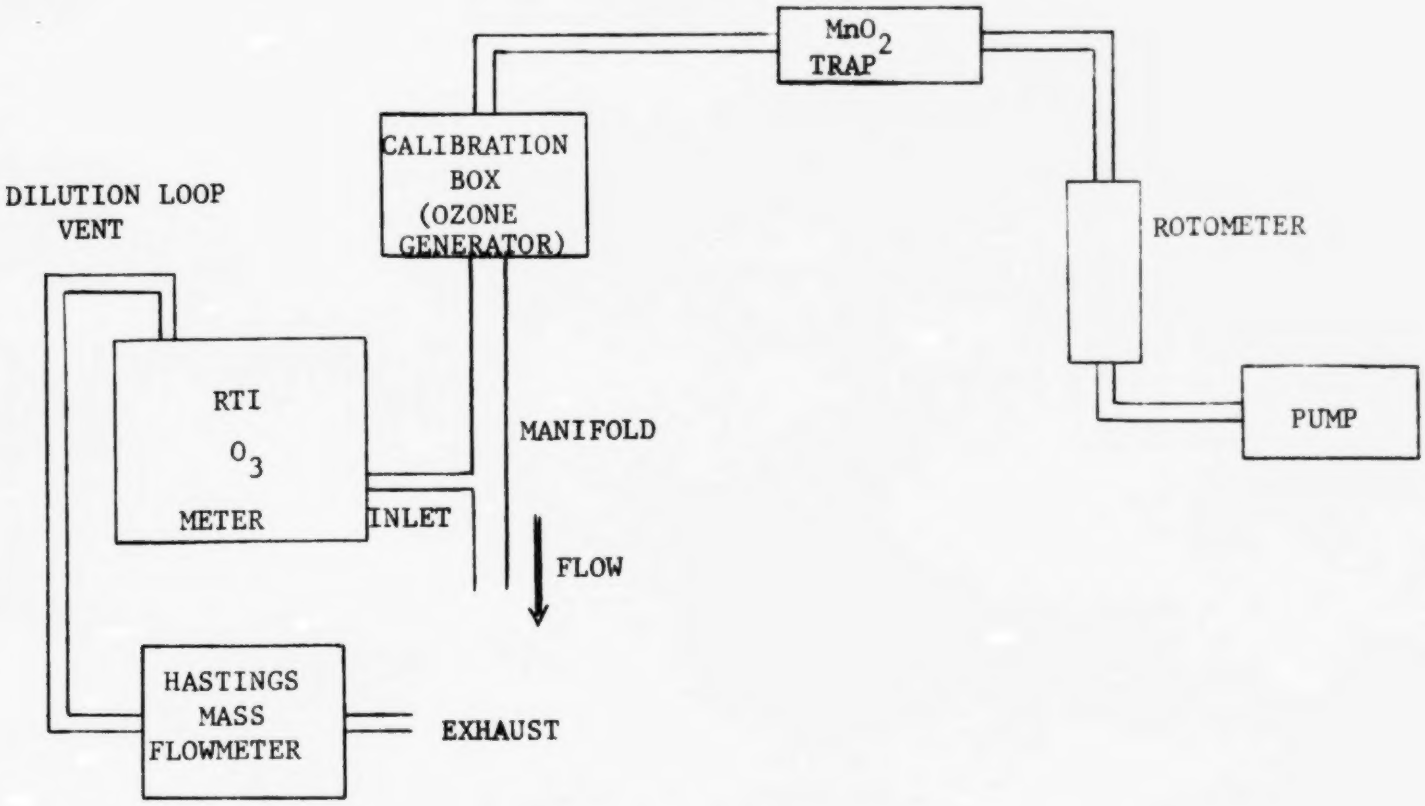

MnO_2
TRAP
CALIBRATION
BOX
(OZONE
GENERATOR)
DILUTION LOOP
VENT
ROTOMETER
RTI
O_3
METER
MANIFOLD
PUMP
INLET
FLOW
HASTINGS
MASS
FLOWMETER
EXHAUST

FIGURE 7. TEST SET-UP FOR MEASURE MODE FLOW-RATE CHARACTERISTICS

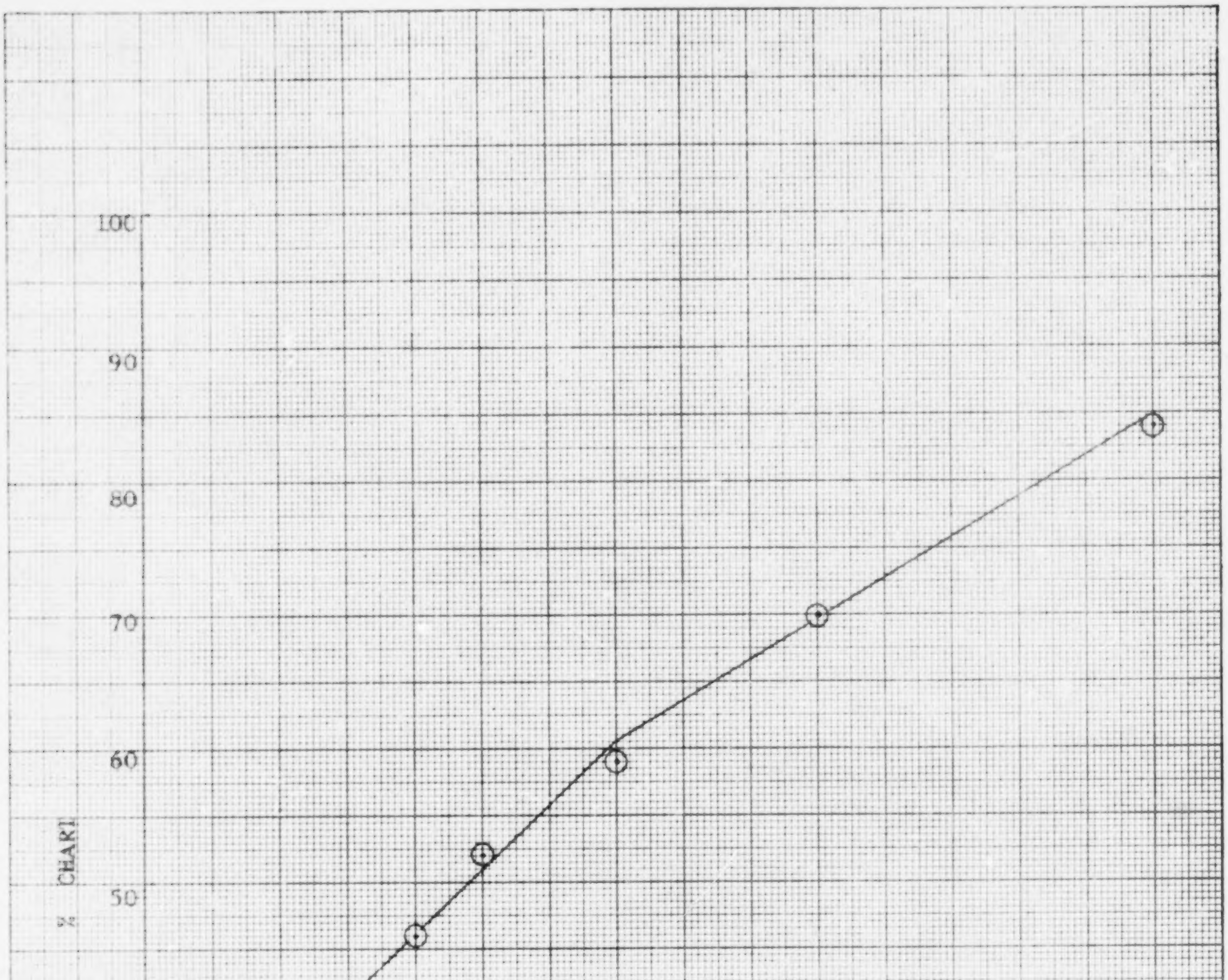


FIGURE 8. RELATIONSHIP BETWEEN FLOW RATE AND SIGNAL OUTPUT

One other characteristic of the instrument, which is a function both of disc and disc chamber, is the effect of total flow rate through the chamber. Table 4 gives the signal obtained from the indicated volume of ozonized air passed through the disc chamber with no recirculation of the sample.

Table 4

TOTAL FLOW RATE DEPENDENCY OF DISC CHAMBER

Air (ml/min)	Signal
200	6.7
300	7.2
400	7.2
500	7.1
600	7.0
700	6.9
800	6.7

Thus, there is range of flow rates giving essentially the same signal for a given concentration of ozone, which extends from about 250 ml/min to 600 ml/min. As would be predicted, however, when sample air is recirculated the fraction of the total flow which consists of outside sample will determine the magnitude of the signal. This is shown in data of Table 5.

Table 5

SAMPLE FRACTIONAL FLOW RATE DEPENDENCY OF DISC CHAMBER

Sample Flow (ml/min)	Total Flow over Disc (ml/min)	Signal
100	600	6.2
100	500	6.5
100	400	8.2
100	300	9.2

3.6.6 Typical Signal Responses -- As was discussed in the section on the chemiluminescent sensor, the transient response of the disc to ozone is a function of its immediate past exposure. For the condition where it is assumed that the proper activation period has been carried out, the two significant types of responses are illustrated in Figs. 9 and 10. The condition for extended exposure to ozone free air is illustrated in Fig. 9. The significant effect is the fast rise time of the signal and large overshoot. The other distinct effect caused by a short time of exposure to clean air between samples of ozone is shown in Fig. 10. This is characterized by the over-damped response to the signal. The ozone concentration for these two examples was on the order of 30 pphm. The overshoot condition is evident for ozone free exposure times on the order of 10 minutes or greater.

An example of a typical response for the instrument while in the 4 min. cycle sampling mode is given in Fig. 11.

The true dark current for the photomultiplier tube is observed when the disc housing shutter is fully closed. This provides for a good check on the tube condition (assuming no light leaks) and provides, essentially, a zero output signal reference level, which may be adjusted to zero by means of the offset control.

The signal from the chemiluminescent disc under conditions of zero O_3 depends again on the immediate past exposure history. In general, once the disc has been exposed to ozone, it requires on the order of hours to decay to the original "dark disc current". This is essentially an exponential decay rate.

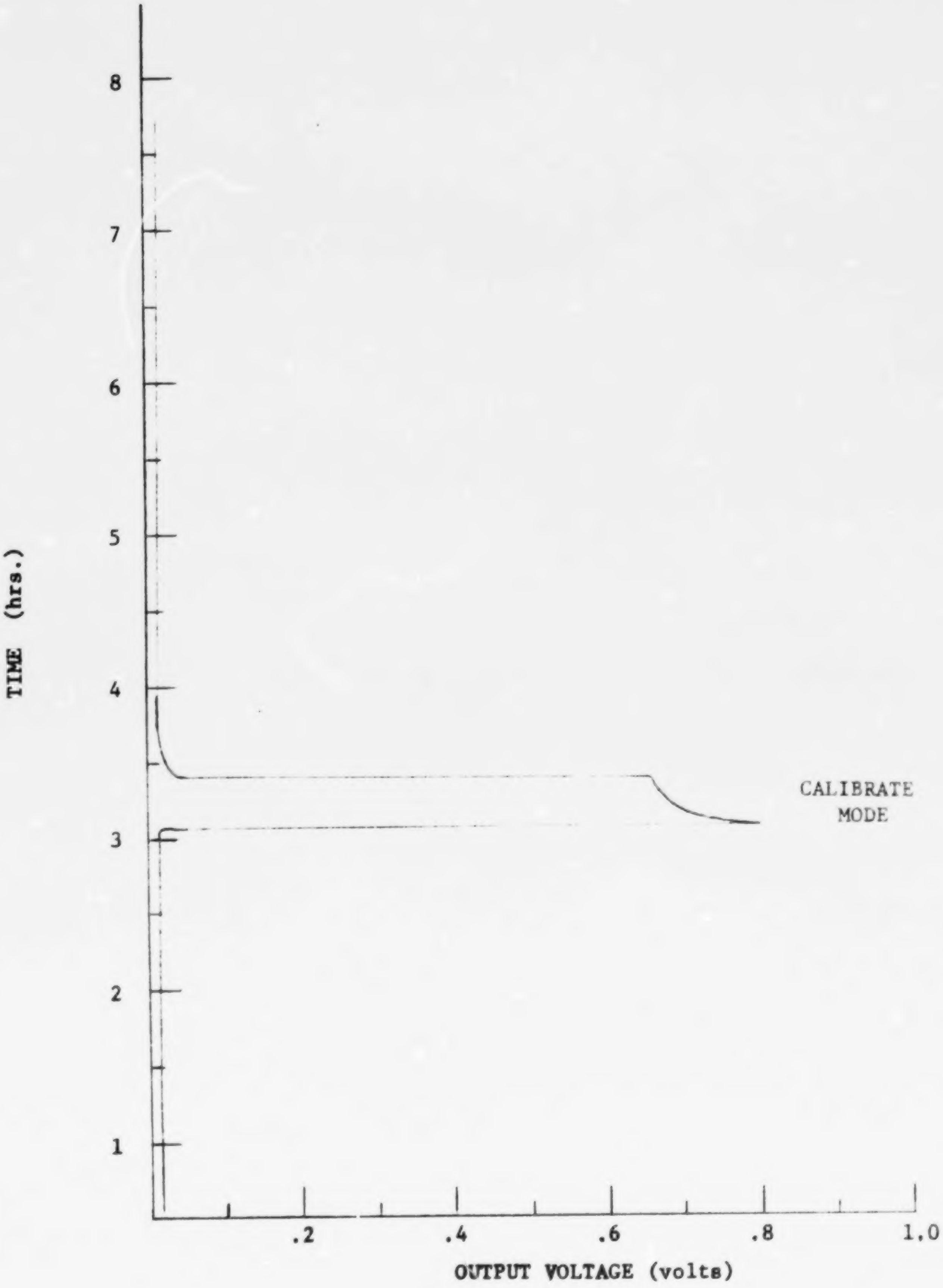


FIGURE 9. INSTRUMENT RESPONSE-6 HOUR CALIBRATION MODE WITH NO EXTERNAL OZONE

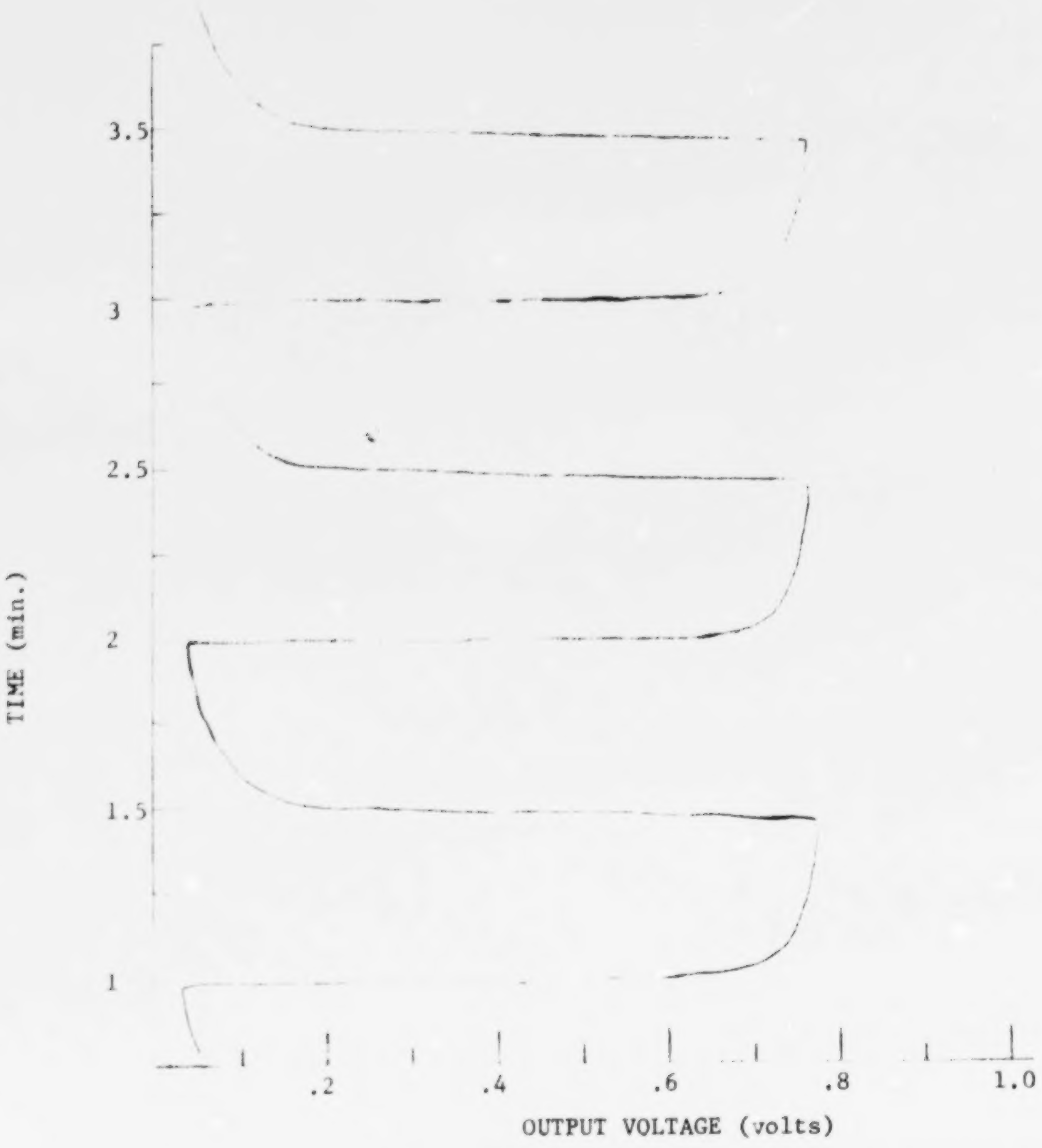


FIGURE 10. INSTRUMENT RESPONSE-30 SECONDS ON AND OFF CALIBRATION PERIODS WITH NO EXTERNAL OZONE.

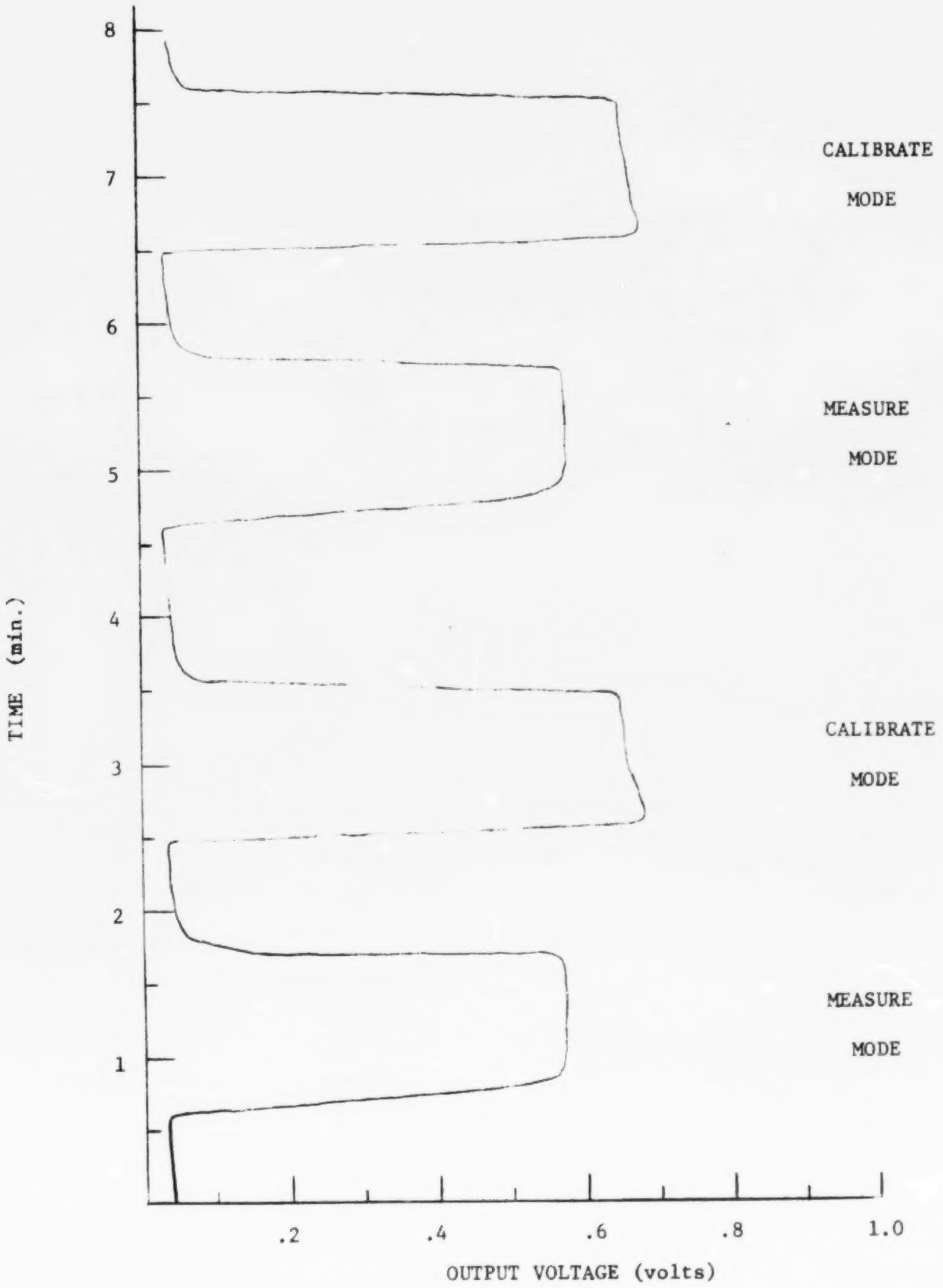


FIGURE 11. INSTRUMENT RESPONSE - SAMPLE MODE MADE WITH EXTERNAL OZONE PRESENT

4.0 DETAILED SYSTEM DESCRIPTION

4.1 General

A functional description of the overall system was given in Section 3.0; reference should be made to this section for clarification. of the individual subsystem functional requirements. Throughout the system, commercially available parts are used where practical. In some cases it was necessary to modify slightly some of the components. All call-out parts may be identified by manufacturer and type by referring to the respective section in the parts list (see appendix).

4.2 Plumbing Subsystem

A detailed diagram of the plumbing subsystem is shown in Fig. 12. In this diagram the functional location of all significant components are shown, along with the type of tubing, fitting, etc. A parts layout for the plumbing subsystem is shown in Fig. 13 in which the relative location of all the components are shown.

In the RUN mode, gases are pulled through the sample air inlet port; during the CALIBRATE mode, gases are pulled through the calibrate air inlet port and through the drying tower. This latter operation removes moisture from the intake air and destroys all of the ozone. Both the sample and calibrate gases follow common paths after passing point (7A). Only one of the two ports is open at any given time. At point (7B) the incoming gas (100 ml/min) is mixed with the dilution air (500 ml/min) and passed through the light rejection coil into the detector unit. The light rejection coil is a single turn of glass tubing--covered with black heat-shrinkable vinyl tubing. This device reduces to an acceptable level the amount of external light entering through the entrance port. The gas passes over the chemiluminescent disc, through another drying tower, flowmeter, valves and pump. Part of the exhaust air is directed to form the dilution flow.

Flowmeters are installed in both the total flow and dilution flow lines for adjustment and monitoring. These meters have a standard accuracy of ± 10% of maximum scale from 100% to 10% of scale reading. The calibration curve is shown in Fig. 39, in Appendix C.3, see this section also for instructions for proper set-up procedure. Three precision vernier control valves are used for this purpose. The total flow and fine dilution valves are located on the front panel of the instrument.

All parts of the system between the sample inlet port and the detector are constructed of either glass or teflon in order to prevent the destruction of ozone. Soft copper and tygon tubing, brass tubing fittings and brass valves are used where contamination is not a problem.

A 5 to 1 dilution system is used to prolong the life of the disc and to reduce the effects of humidity. A commercial desiccant, Drierite with approximately 1" of MnO_2 in the center or outlet end of each tower are used to remove the moisture and destroy any ozone present, respectively.

Because of the type of single pump system and dilution line configuration it is necessary to maintain a constant pressure at the inlet port. If the inlet pressure changes, the total flow remains constant while the dilution flow increases or decreases to compensate for the change in sample flow due to the pressure change.

The following data shows the effectiveness of the rotameter float or the vernier scale as an indication of air flow. The dilution flow was manually changed and then returned to 100 ml/min as indicated by a mass flow meter located at the inlet sampling port. The float position and vernier were then read. Total flow was held constant.

	Float	Vernier	
Day 1	36	46.3	
	36	48.7	vernier = ± 5%
	36	45.3	
	36	46.5	
	36	47.1	
	36	45.4	
	36	46.1	
Day 2	36	45.8	

Adjusting the flow as indicated by the float, the error from 100 ml/min shown by the mass flow meter was ≈ 2 percent.

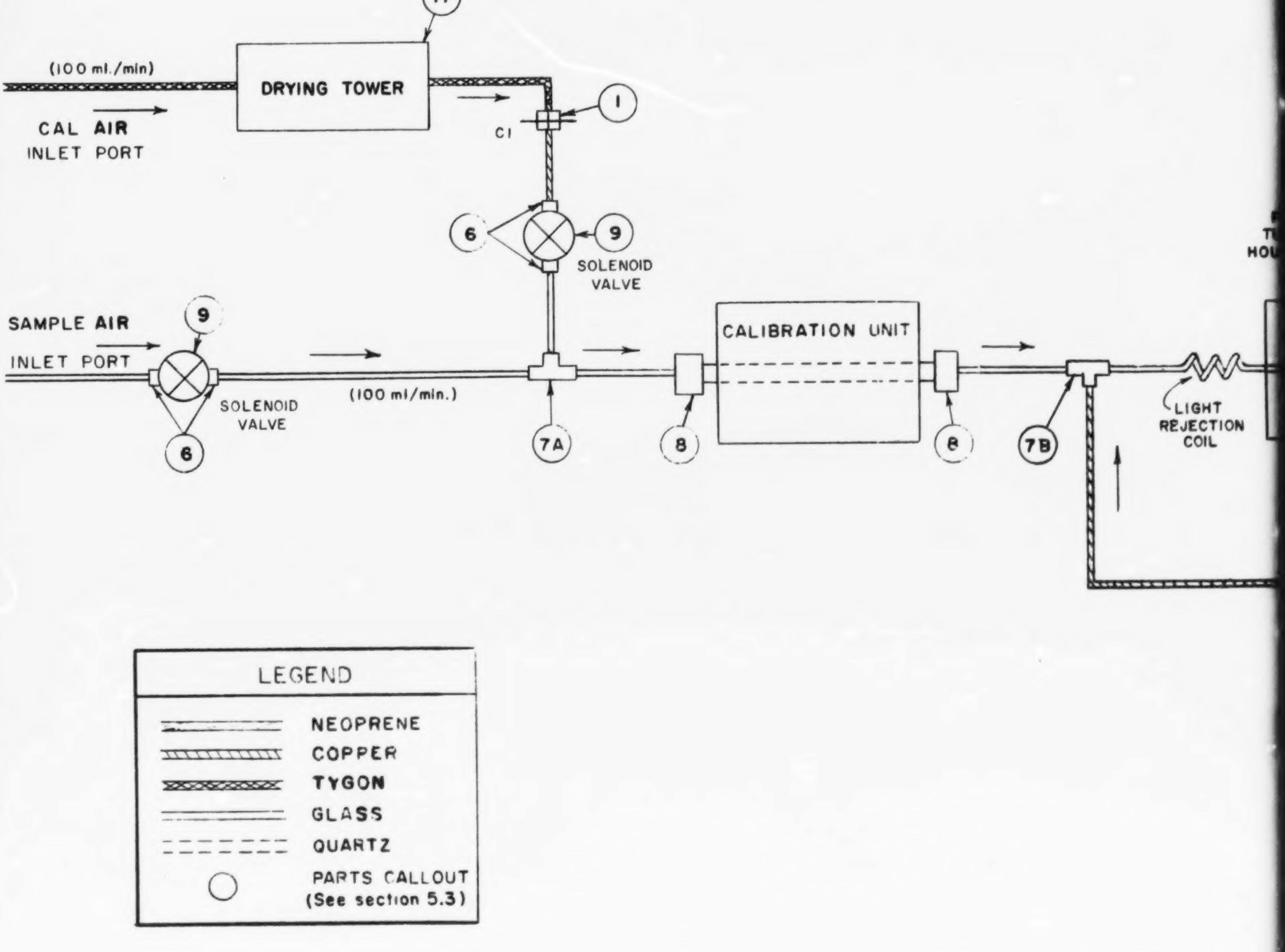
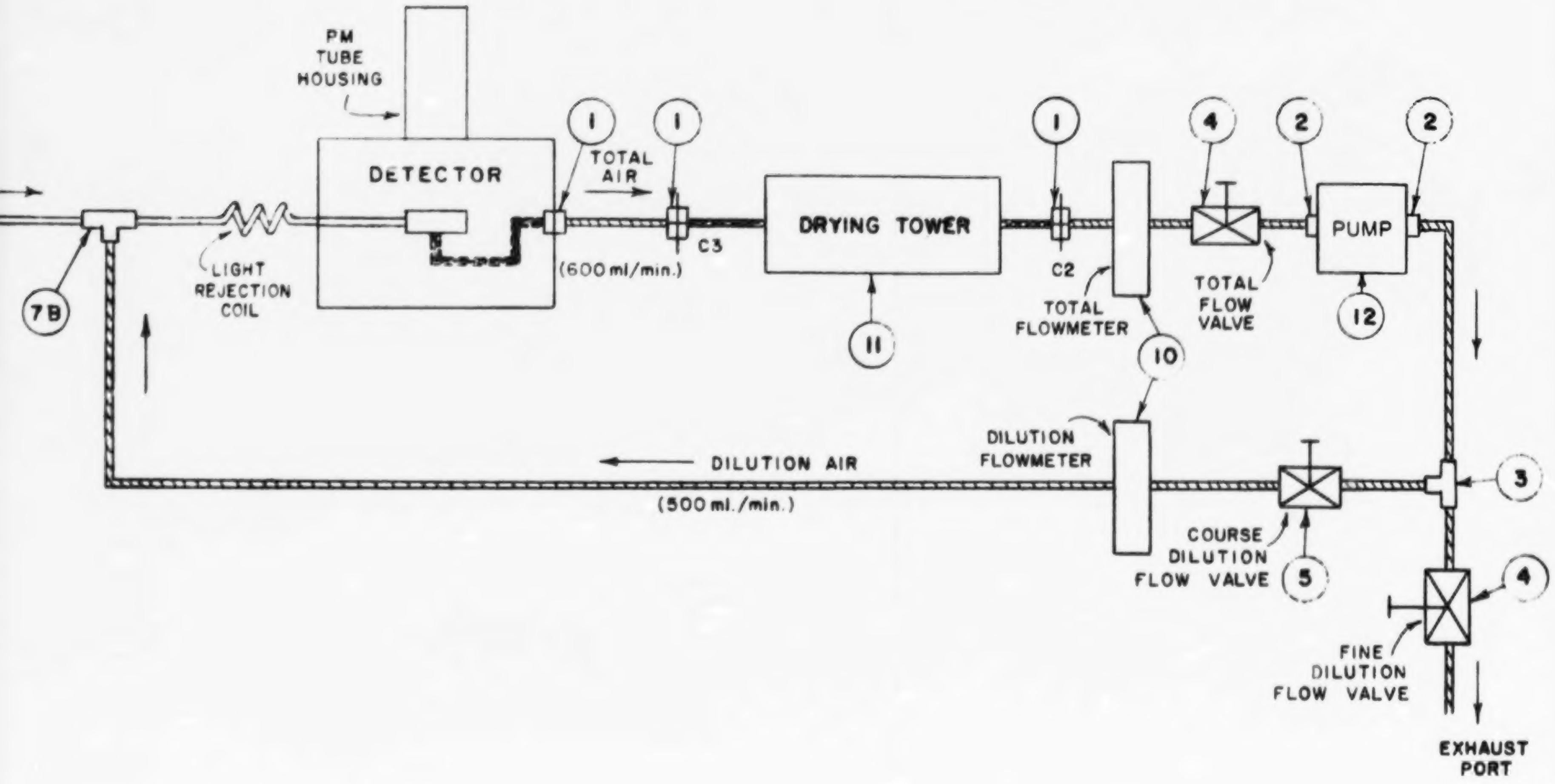

(100 ml./min)
DRYING TOWER
11
1
C1
CAL AIR
INLET PORT
6
9
SOLENOID
VALVE
SAMPLE AIR
INLET PORT
9
SOLENOID
VALVE
6
(100 ml/min.)
7A
CALIBRATION UNIT
8
8
7B
LIGHT
REJECTION
COIL
T
HOU
LEGEND
NEOPRENE
COPPER
TYGON
GLASS
QUARTZ
PARTS CALLOUT
(See section 5.3)

FIG. 12 PLUMBING SUBSY

A


PM TUBE HOUSING
DETECTOR
LIGHT REJECTION COIL
7B
1
1
1
TOTAL AIR
(600 ml/min.)
C3
DRYING TOWER
11
C2
TOTAL FLOWMETER
4
TOTAL FLOW VALVE
2
PUMP
2
12
10
DILUTION FLOWMETER
DILUTION AIR
(500 ml./min.)
3
COURSE DILUTION FLOW VALVE
5
4
FINE DILUTION FLOW VALVE
EXHAUST PORT

PLUMBING SUBSYSTEM

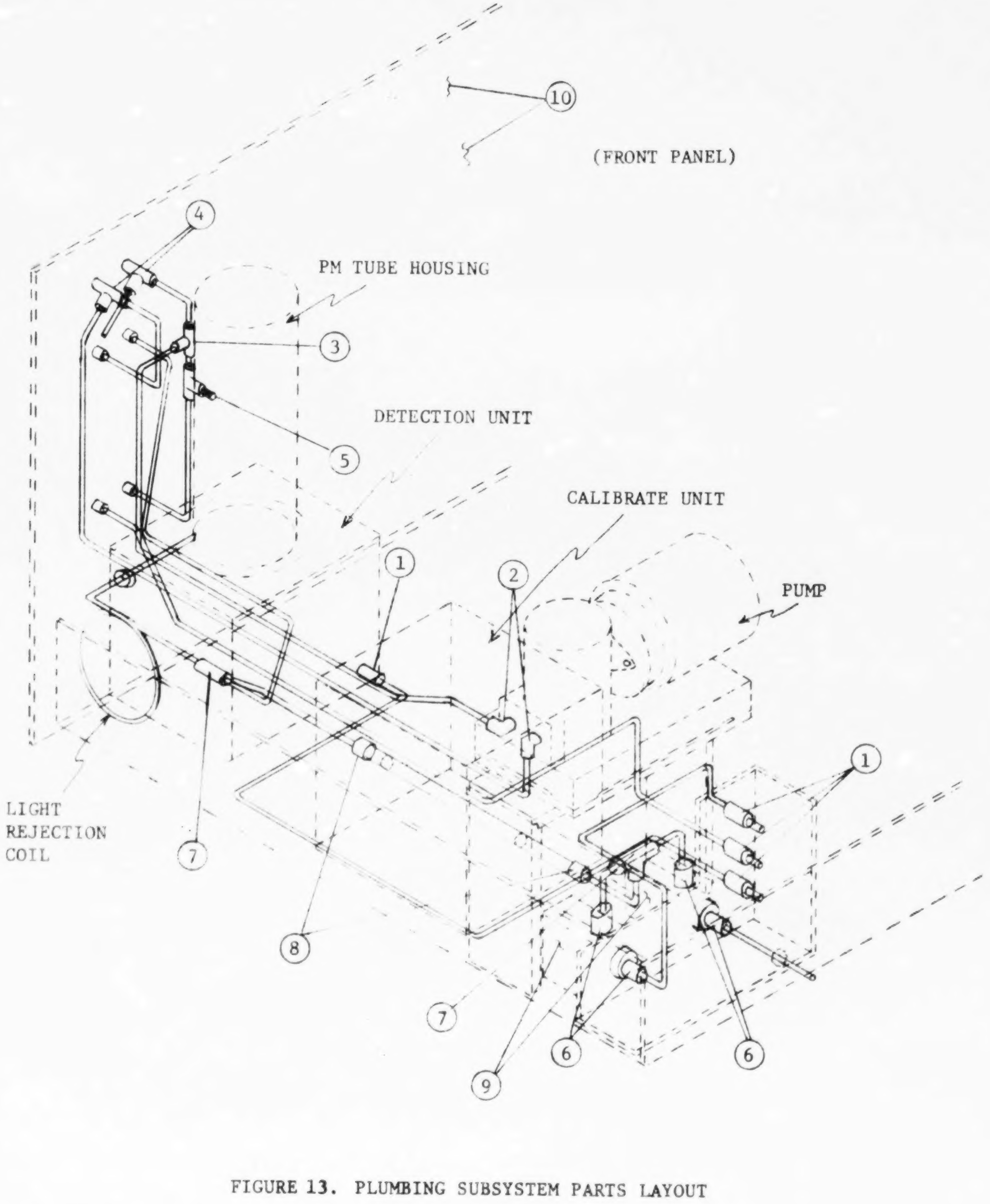

10
(FRONT PANEL)
4
PM TUBE HOUSING
3
DETECTION UNIT
5
CALIBRATE UNIT
1
2
PUMP
1
LIGHT
REJECTION
COIL
7
8
7
6
6
9

FIGURE 13. PLUMBING SUBSYSTEM PARTS LAYOUT

4.3 Detector

A cross sectional view of the detector assembly showing the principal components is shown in Fig. 14. The location of the detector unit in the system is shown functionally in Fig. 1, and the associated plumbing is shown in Fig. 12. The principal components of the detector are the photomultiplier tube (PM) and HV supply, disc chamber and associated plumbing. The chamber is designed so that the inlet air enters the chamber tangentially to the disc and follows a spiral-like flow over the disc, passing through the exhaust port which is located in the center of the disc chamber. A pictoral representation of this is given in Fig. 15. The top of the chamber consists of a quartz window sealed to the chamber, thus providing an air-tight chamber.

Light entering the chamber by the inlet port is reduced to an acceptable value by means of a loop in the inlet glass tubing. The loop is encased in black vinyl heat-shrinkable tubing. Black rubber tubing satisfies the requirements for the exit port.

The cutaway view of the PM tube and housing in Fig. 14 shows the placement of the special grounding braid located between the tube near the cathode end and the MU-metal shield. The latter shields against stray electric and magnetic fields. The braid reduces noise due to static charge buildup on the tube. This is an addition to the standard PM tube housing. The separation distance between the PM tube cathode and the chemiluminescent disc is approximately 1/2 inch. See Appendix C.10 for details on tube handling.

The cathode of the PM tube is positioned approximately flush with face of the PM tube housing bolt flange. A circuit diagram of the

PM tube base wiring is shown in Fig. 16. The tube is an EMI Type 9558C selected for dark current $< 10^{-9}$ amps. The high voltage (HV) for the PM tube is generally set for the value which yields a gain = 200.

A compilation of the PM tube characteristics for both the 9558C and the 9750 type is given in Table 6. This includes the factory specifications and the measured values for dark current. The ratio of measured to rated dark current was approximately 3/1 which was in line with the expected increase in PM tube dark current due to increased temperature. The factory rated value is run at 20°C while the units in the laboratory were operated somewhat above this level.

The signal-to-dark current ratio, which was used as a measure of comparative sensitivity for the PM tubes, was measured on the same unit, same disc, etc., with no changes in conditions within practical limits.

The high voltage supply is a Power Designs Model 2K-10 with front panel controls which allow for precise selection of the high voltage value. A cover is provided for this unit so that the voltage controls will not inadvertently be changed. The unit is so designed so that both the high voltage and primary power ON switches are left in the ON positions and the power for the entire instrument controlled by the one power switch. A test was made on 5 of the HV supplies to determine the accuracy of the voltage setting controls. This was done by setting the controls for the 500, 750 and 1000 volt levels in turn and measuring the true output with a Fluke Model 895A DC null voltmeter. The results are shown in Table 7.

TUBE 9558C SERIAL #	DARK CURRENT (RATED)	DARK CURRENT (MEASURED)	RATIO OF QUOTED TO MEASURED	HIGH VOLTAGE (FOR GAIN OF 200)	CATHODE SENS.	SIGNAL TO DARK CURRENT RATIO	COLOR SENSITIVITY		
							B	R	IR
11781	2.6	6.8	2.62	1930	180	54.0	10.3	52	4.2
11959	0.8	2.4	3.00	990	94	100.0		26	0.4
11987	1.7	4.7	2.76	1130	118	16.0	8.2	41	1.6
11814	3.0	10.0	3.33	1970	170	23.0	9.0	55	5.8
11994	0.5			1030	110	180-200	7.4	36	1.2
11312	2.2	6.2	3.55	1340	96	16.7	7.0	34	2.6
20002	2.8	0.5	0.178	1110	98	128.0	7.1	30	0.6
TUBE 9750									
5173	0.1	.45	4.5	860	54	100.0			

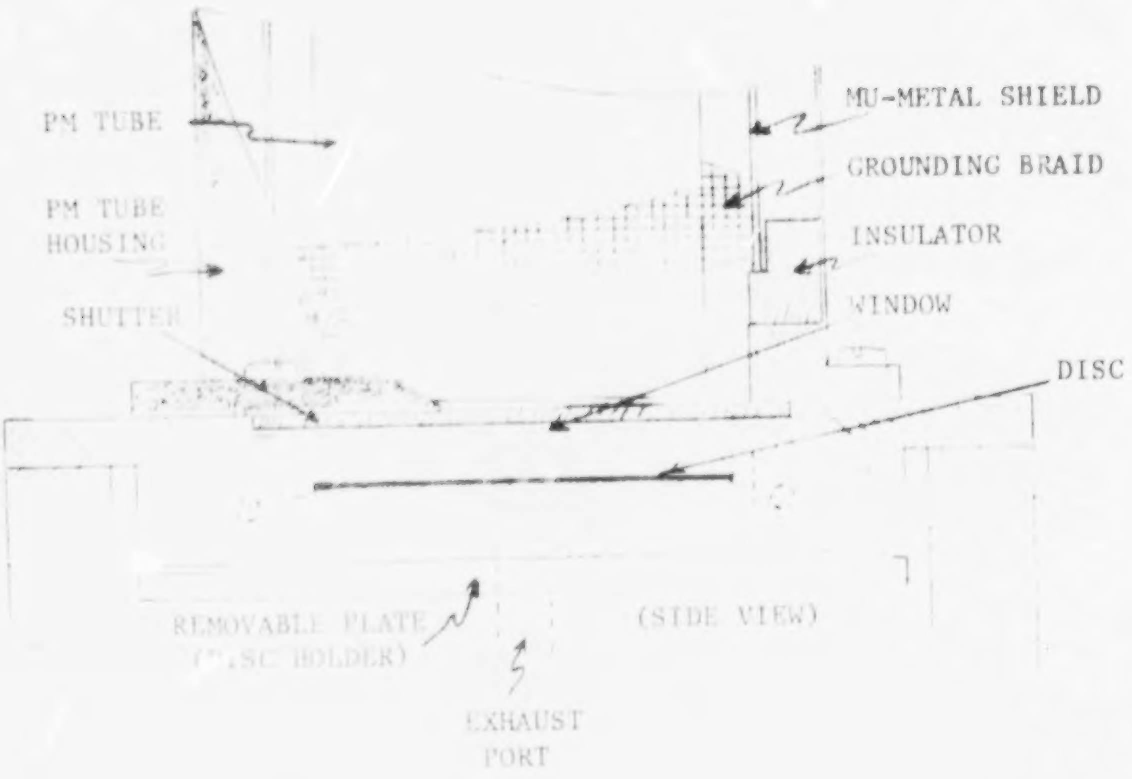
TABLE 6. PHOTOMULTIPLIER TUBE CHARACTERISTICS

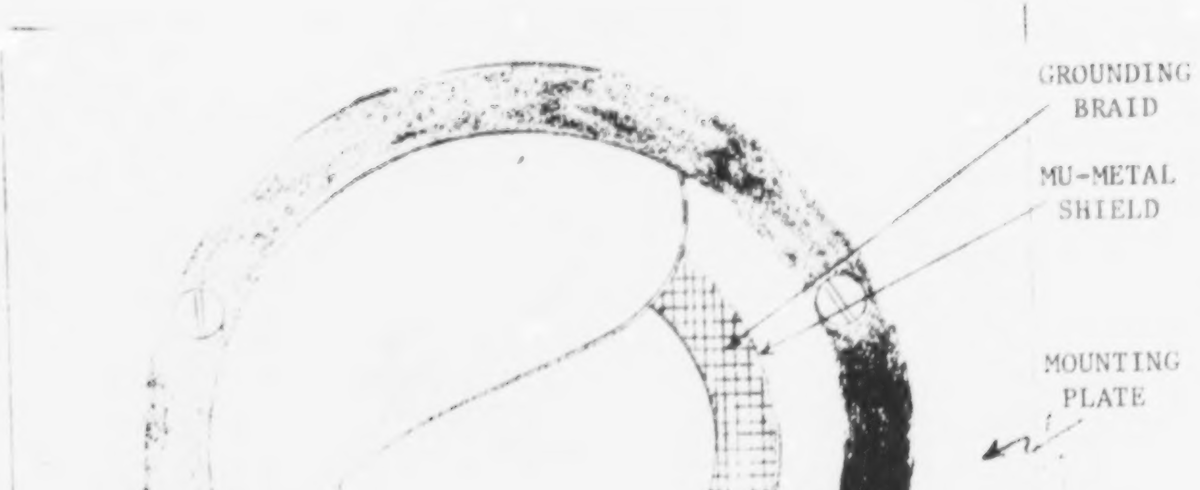
Table 7

HV POWER SUPPLY SETABILITY TEST

Unit Number	Voltage Setting 500	750	1000
902151	501.4	751.5	1001.8
902166	501.6	751.9	1002.2
902185	501.94	752.5	1002.985
902193	501.65	751.94	1002.28
902163	501.43	751.71	1001.96

A shutter is incorporated in the disc housing between the quartz window and the cathode of the PM tube. The primary purpose of the shutter is to facilitate the measurement of the PM tube dark current. In addition it is used to protect the tube from external light when the disc is replaced. Access to the disc is through the door on the front panel. A miniature lab jack is used to raise and lower the disc holder. An interlock circuit, designed to prevent inadvertent exposure of the PM tube to excess light, gives visual indication for the fully open and fully closed conditions for the shutter. When the shutter is in the fully opened position, a mechanical stop prevents opening of the disc access door. A buzzer sounds if the disc access door is opened when the shutter is in any but the fully closed condition. Details on this circuit are given in Fig. 17.


PM TUBE
PM TUBE HOUSING
SHUTTER
MU-METAL SHIELD
GROUNDING BRAID
INSULATOR
WINDOW
DISC
REMOVABLE PLATE (DISC HOLDER)
EXHAUST PORT
(SIDE VIEW)


GROUNDING BRAID
MU-METAL SHIELD
MOUNTING PLATE
PLATE OPENING
DISC
PM TUBE

(TOP VIEW)

FIGURE 14. DETECTOR ASSEMBLY

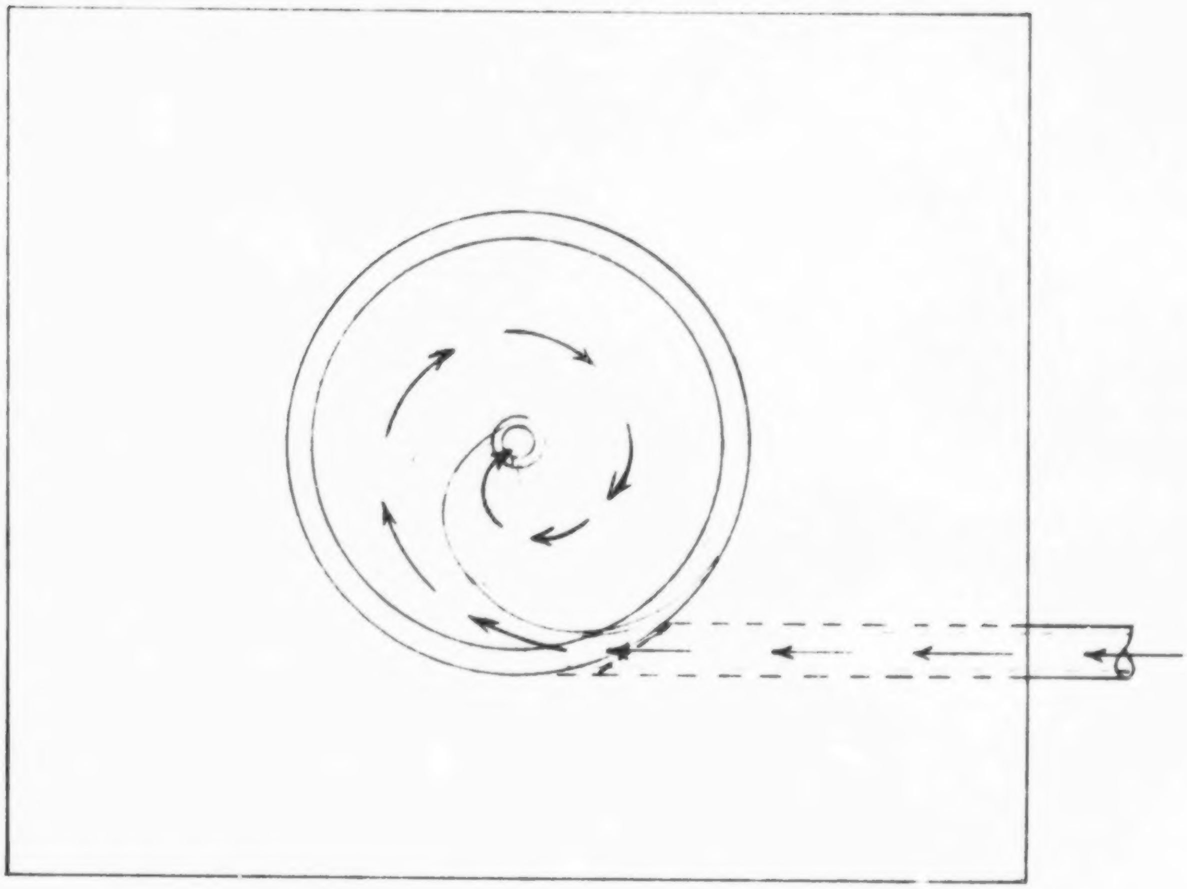
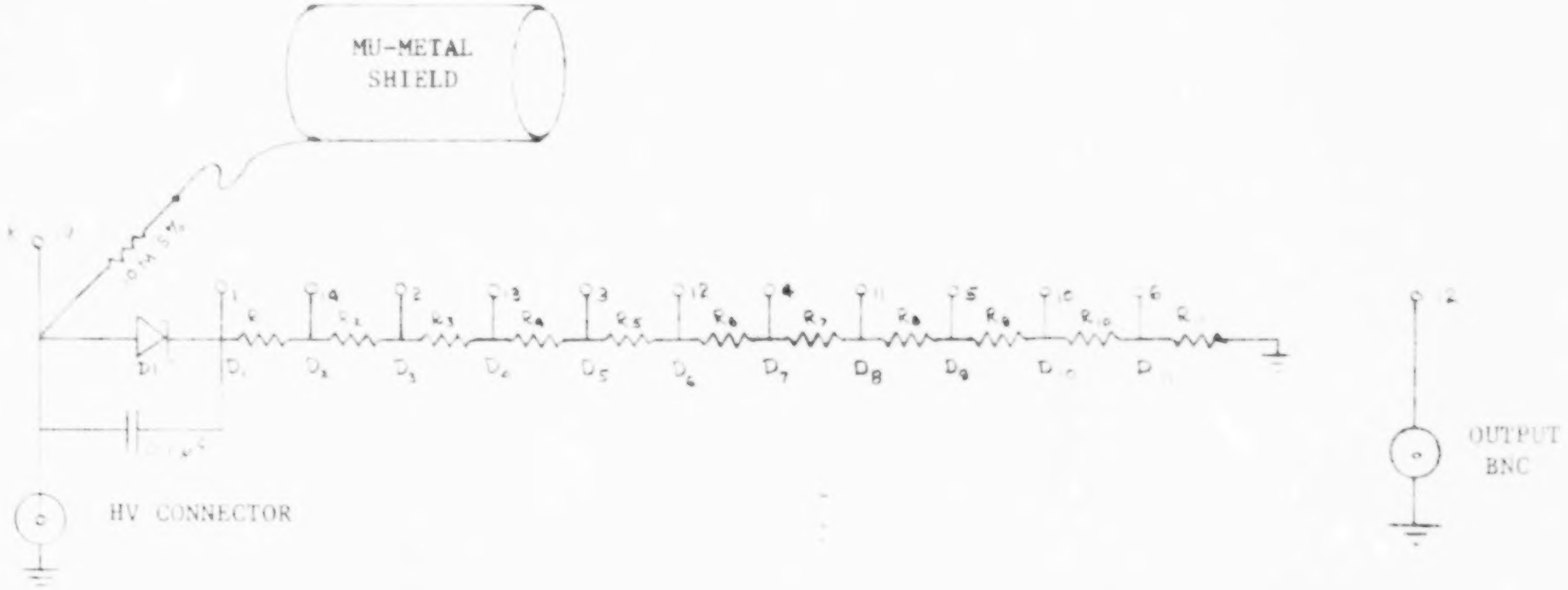


FIGURE 15. AIR FLOW PATTERN IN DISC CHAMBER


MU-METAL
SHIELD
K
D1
1
14
2
13
3
12
4
11
5
10
6
12
R
R_2
R_3
R_4
R_5
R_6
R_7
R_8
R_9
R_{10}
R_{11}
D_1
D_2
D_3
D_4
D_5
D_6
D_7
D_8
D_9
D_{10}
D_{11}
HV CONNECTOR
OUTPUT
BNC

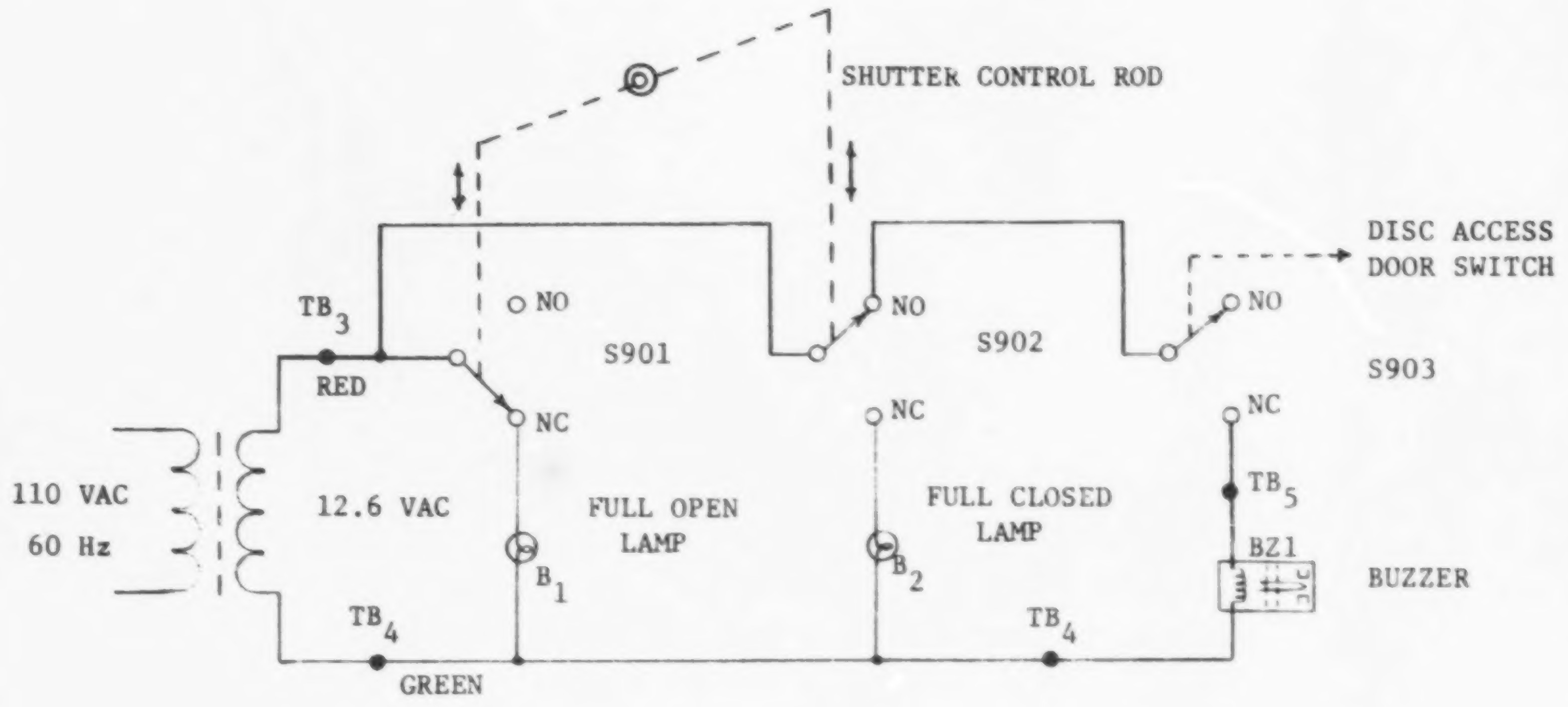
R_1 - R_{11} - 200K, 1% METAL FILM

D1 - ZENER DIODE 1N5276B

V_Z = 150 V

V_{ZT} = 0.85 mA

FIGURE 16. PM TUBE HOUSING WIRING DIAGRAM


SHUTTER CONTROL ROD
DISC ACCESS DOOR SWITCH
TB$_3$
RED
NO
NC
S901
NO
NC
S902
NO
NC
S903
110 VAC
60 Hz
12.6 VAC
FULL OPEN LAMP
B$_1$
FULL CLOSED LAMP
B$_2$
TB$_5$
BZ1
BUZZER
TB$_4$
GREEN
TB$_4$

NOTE: SWITCHES SHOWN WITH SHUTTER OPEN AND DOOR CLOSED

FIGURE 17. INTERLOCK CIRCUIT

4.4 Calibration Unit

In the calibration unit clean air is exposed to a constant amount of ultraviolet radiation from a low-pressure mercury arc lamp. The particular spectral region of interest is around 1850 Å. The resonance line of mercury is 2537 Å; however, enough energy is radiated in the shorter wavelength region to produce the desired ozone level. The calibration unit consists of a low pressure mercury arc lamp, a quartz tube through which the clean air flows, and an adjustable aperture and solenoid controlled shutter. A cutaway drawing of the calibration unit listing the major components, is shown in Fig. 18. Details on lamp replacement and aperture range adjustments are given in Appendix C.5 and C.9, respectively. The level of radiance is controlled and monitored by means of a variac and lamp current meter. Various, but repeatable, levels of O_3 concentration are obtainable with the adjustable aperture. The specific calibration curve for each instrument is included in the front of the manual.

The housing is essentially a sealed unit to preclude the escape of ozone or UV radiation. Because of the thick wall construction, the unit is reasonably stable, thermally. The lamp is left on at all times and the unit is effectively turned on and off by activation of the electrically operated shutter. The particular UV lamp used is rated at 17 mA. To improve stability, the lamps are pre-aged for 400-500 hours, selected for optimum characteristics, and then operated at 10 mA.

The ozone concentration is dependent on lamp temperature, lamp current, aperture setting, and flow rate. The lamp temperature is regulated by the thermal stability of the unit. The result of lamp current variation on the amount of ozone generated in the individual calibration units was determined for a current range of 5 to 18 mA, with a constant aperture setting of 0 (i.e., maximum opening) and air flow rates of 50, 100, 150, 200 and 300 ml/min. This is shown in Fig. 19. The dependency of ozone output as a function of line voltage is shown in Fig. 20 for one flow rate and constant aperture setting. At a flow rate of 100 ml/min, ozone output deviation is 0.6 pphm or 6 percent per volt change in AC line voltage. These values are typical for all instruments. Typical curves for ozone concentration as functions of flow rate and aperture setting are shown in Figs. 21 and 22, respectively.

Attenuating the photon flux incident on the quartz tube by reducing the aperture diameter from 1.0 inch (micrometer set at 0), to 0.5 inch (micrometer set at 10.0) linearly decreases the maximum ozone output of each calibration unit by an average of 37 percent. See Fig. 23 which shows both the low range and high range calibration curve for a typical unit.

The stability of the individual calibration units is within the sensitivity of the monitor and the experimental error of the calibration procedure. Reproducibility error on the order of 6 percent was evident from the calibration data, which also is within the determined repeatability of the experimental procedure.

Ozone generated from the individual calibration units at various air flow rates, source currents and aperture settings was determined by the Neutral Buffered-Potassium Iodide Method and also by comparison to a separate calibrated ozone source after the unit in test was permanently installed in the monitor chassis. The detailed calibration technique is given in Appendix A.

A calibrated ozone generator identical to the installed unit, preceded by an ozone-moisture trap and a mass flow meter, was attached to the sampling port of the ozone monitor being tested (see Fig. 24). Operating the monitor in the sample mode provided comparison data, which was indicative of the final calibration for the installed unit at various aperture settings. The stability and reproducibility of the individual units was also observed.

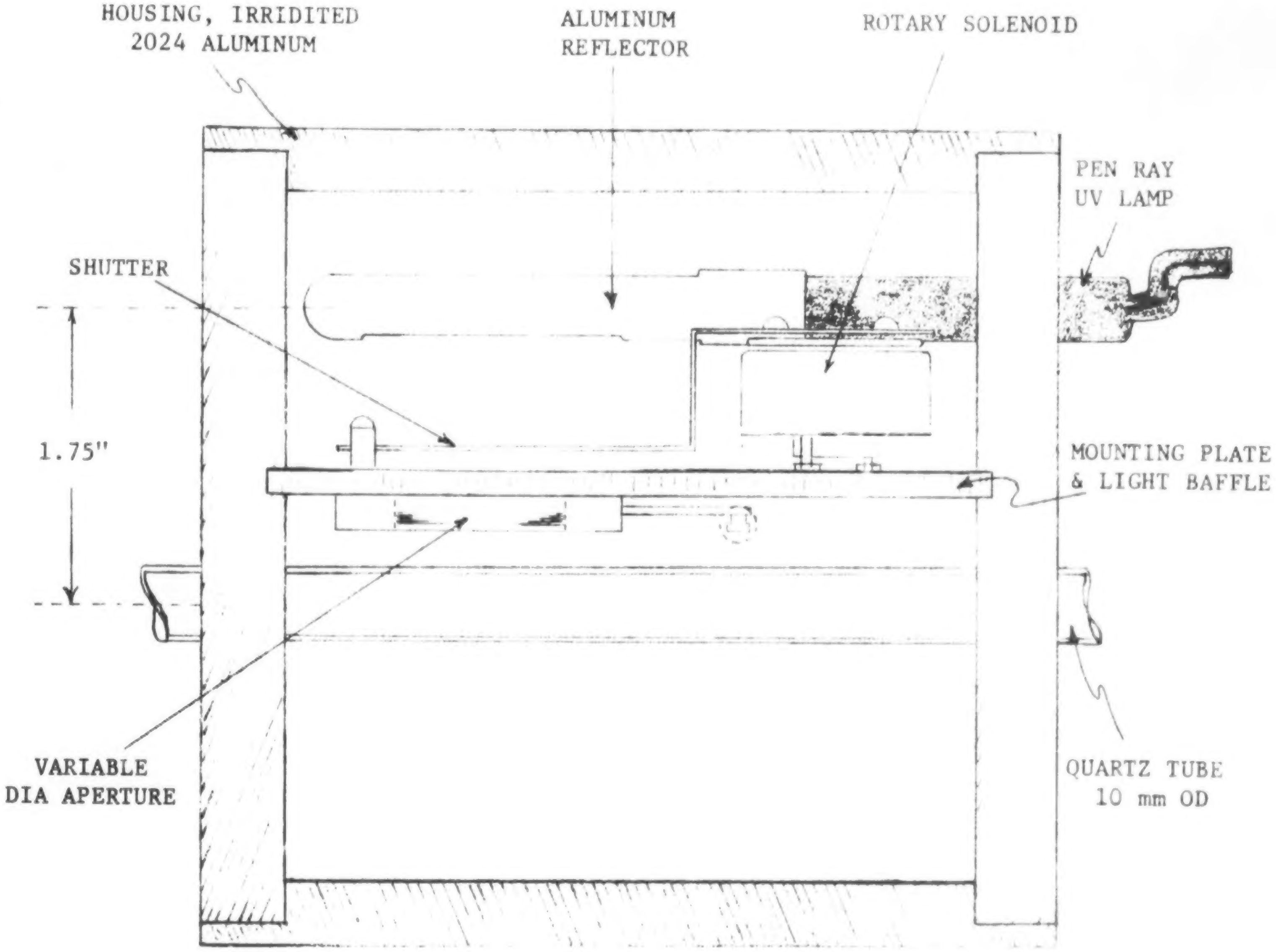

HOUSING, IRRIDITED
2024 ALUMINUM
ALUMINUM
REFLECTOR
ROTARY SOLENOID
PEN RAY
UV LAMP
SHUTTER
1.75"
MOUNTING PLATE
& LIGHT BAFFLE
VARIABLE
DIA APERTURE
QUARTZ TUBE
10 mm OD

FIGURE 18, CALIBRATION UNIT (top view)

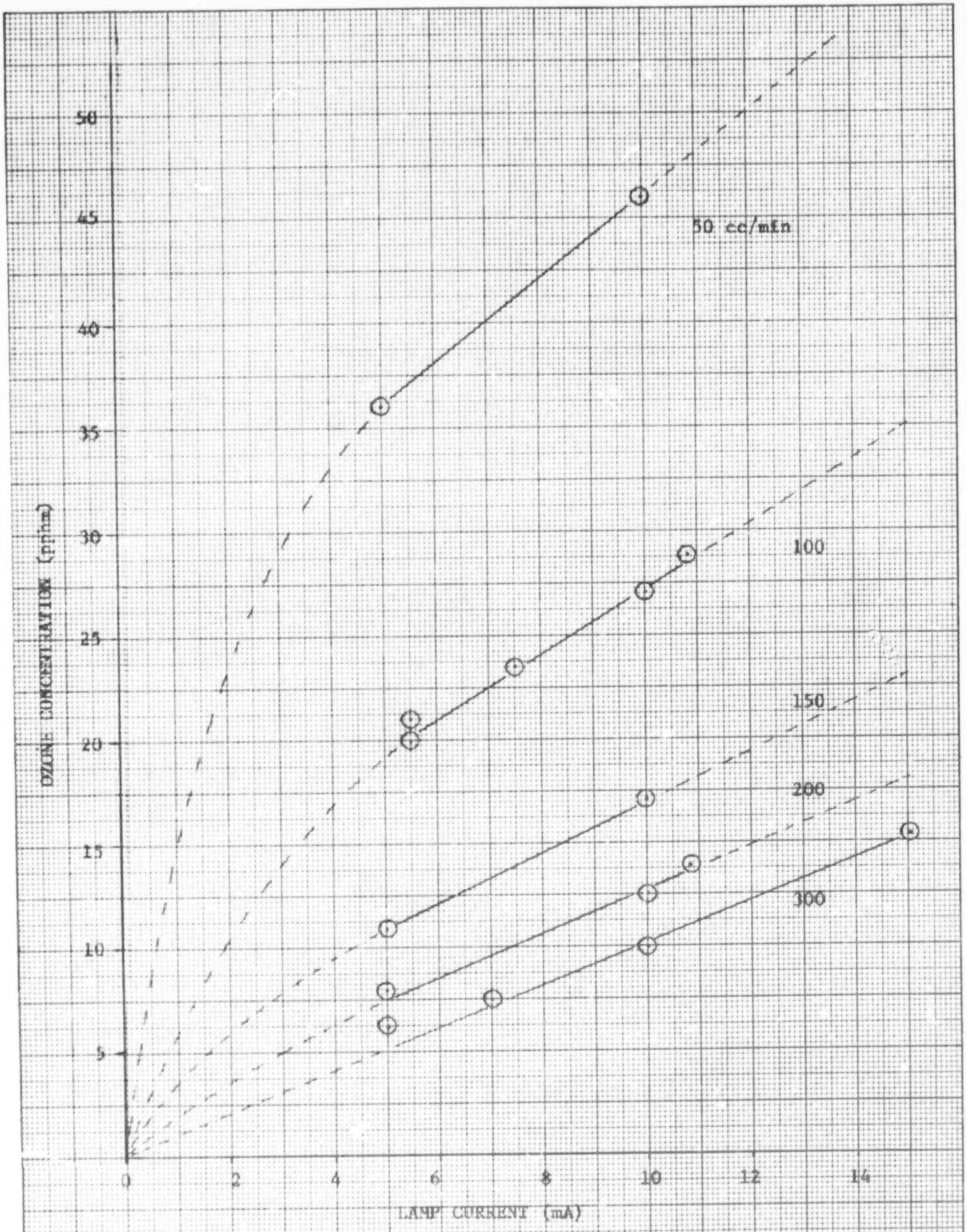


FIGURE 19. OZONE CONCENTRATION AS A FUNCTION OF LAMP CURRENT AND FLOW RATE

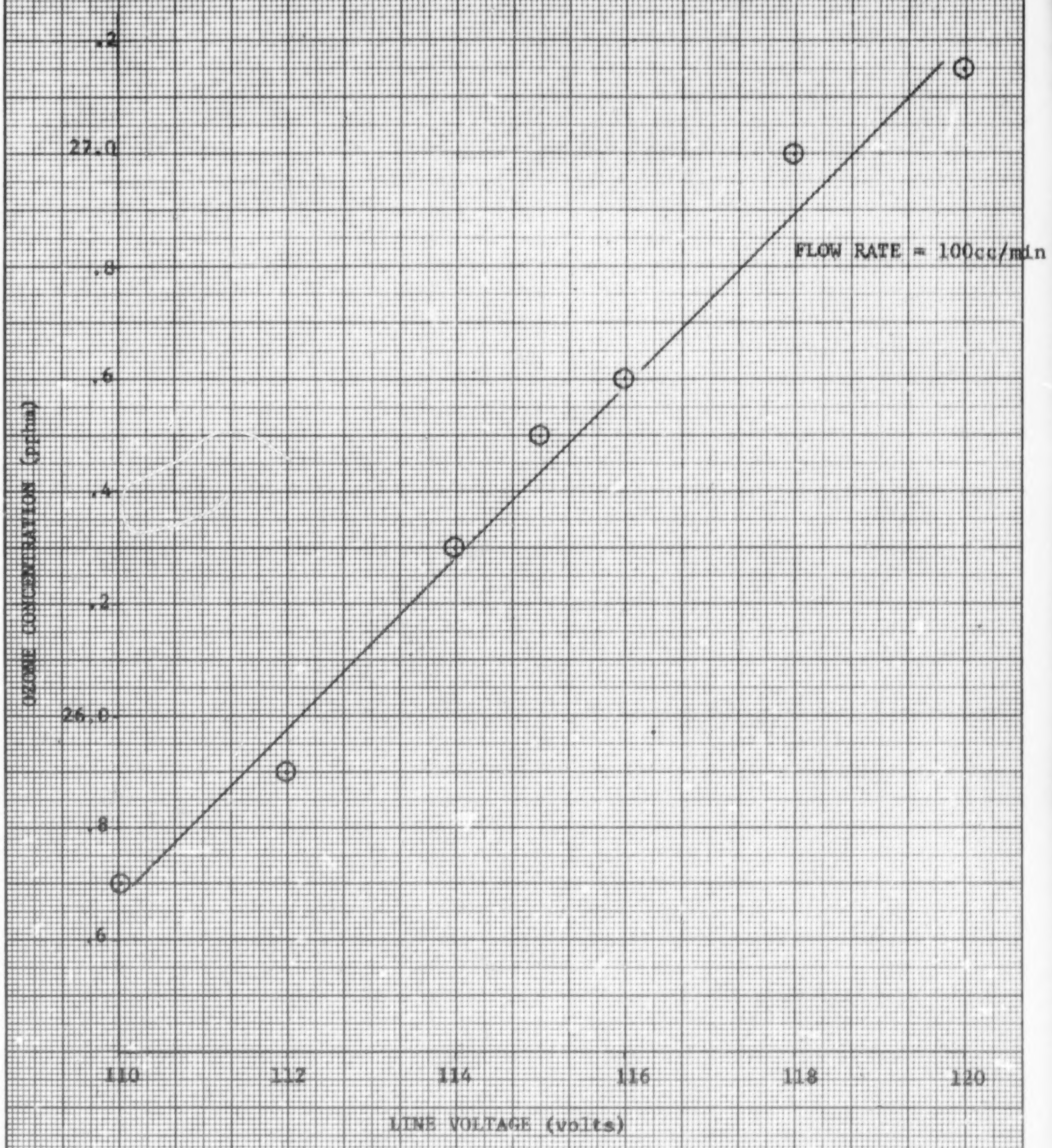


FIGURE 20. OZONE CONCENTRATION AS A FUNCTION OF LINE VOLTAGE

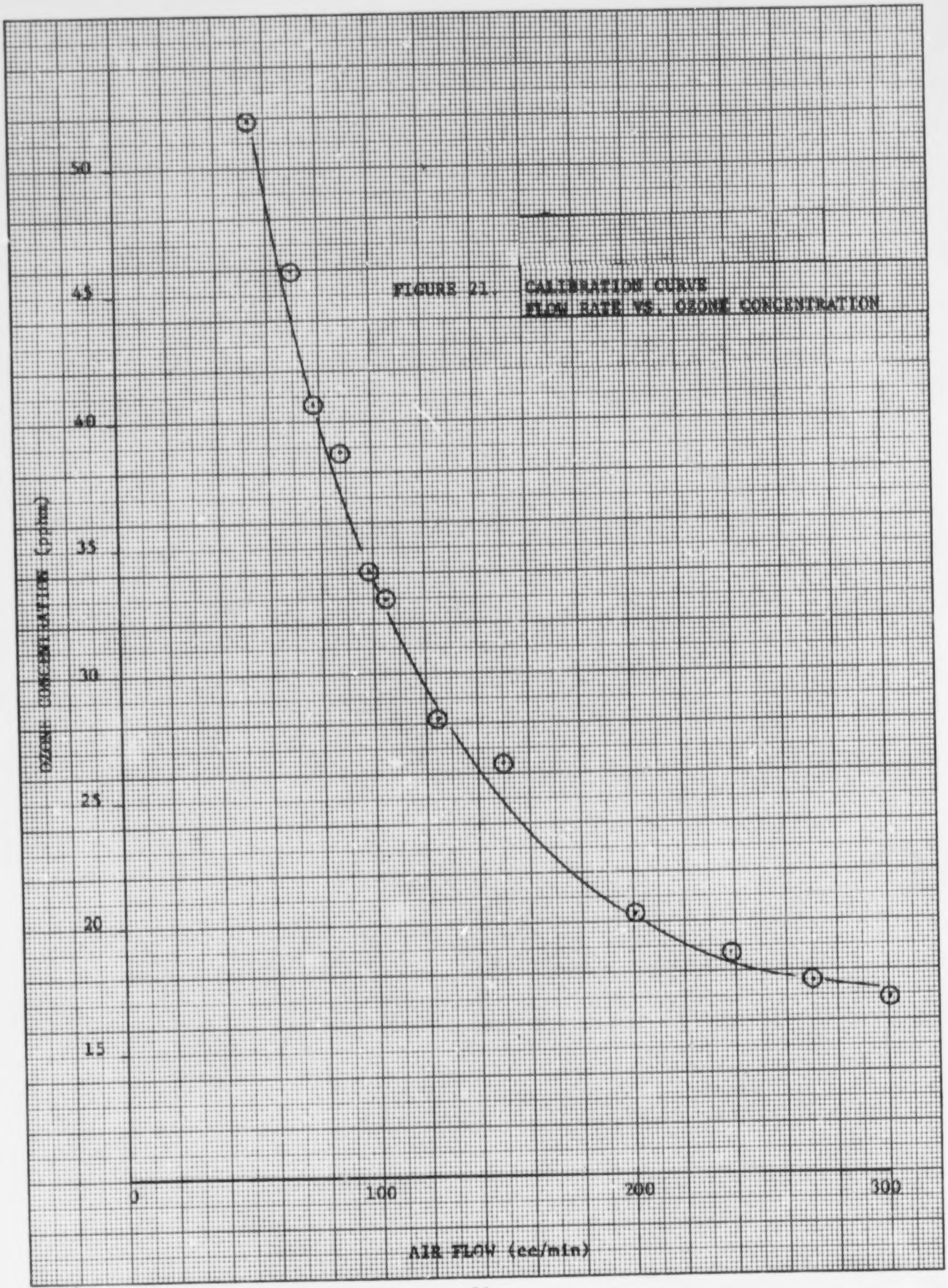


FIGURE 21. CALIBRATION CURVE
FLOW RATE VS. OZONE CONCENTRATION

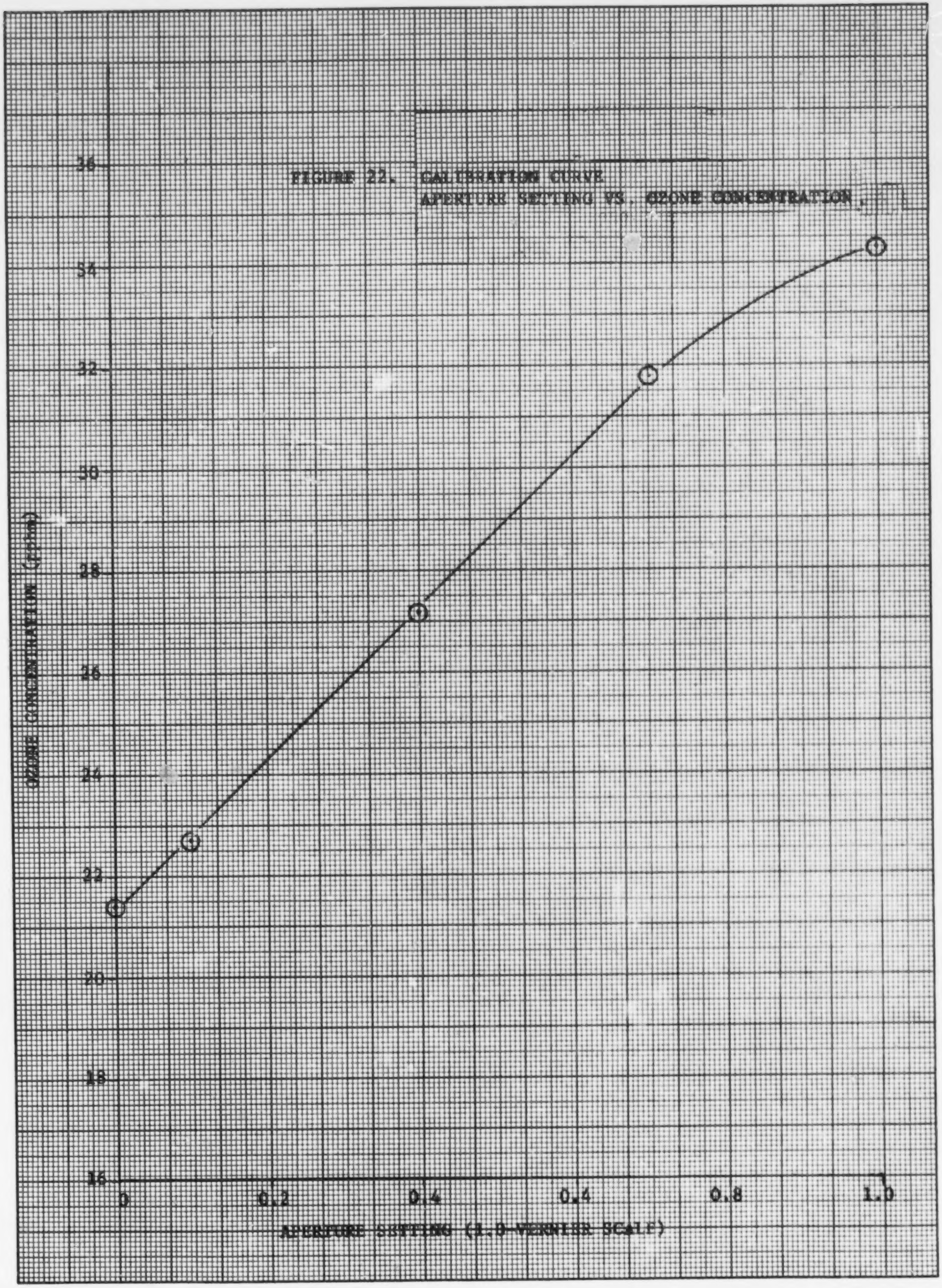


FIGURE 22. CALIBRATION CURVE
APERTURE SETTING VS. OZONE CONCENTRATION.

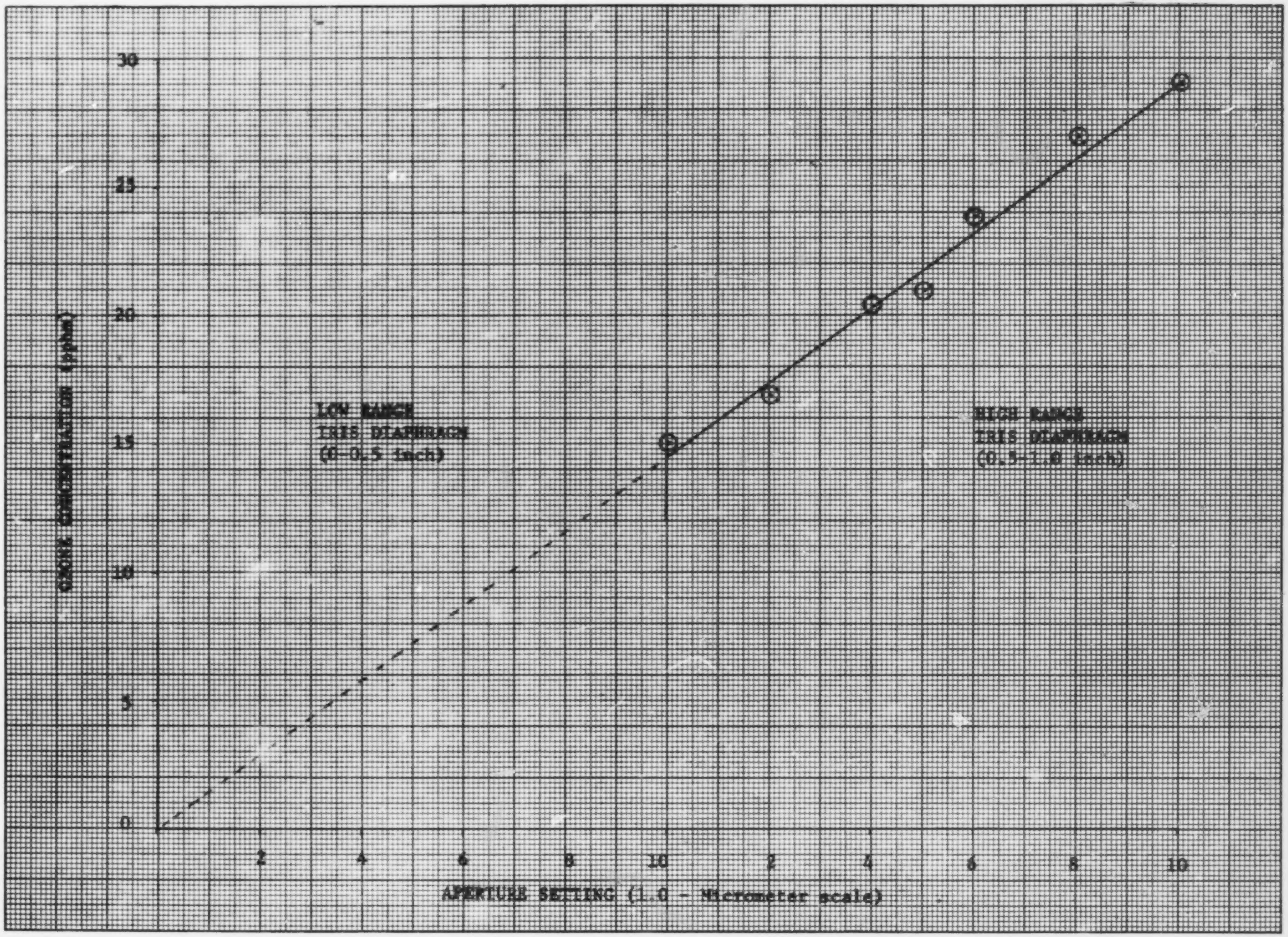


FIGURE 23. TYPICAL FULL RANGE CALIBRATION CURVE

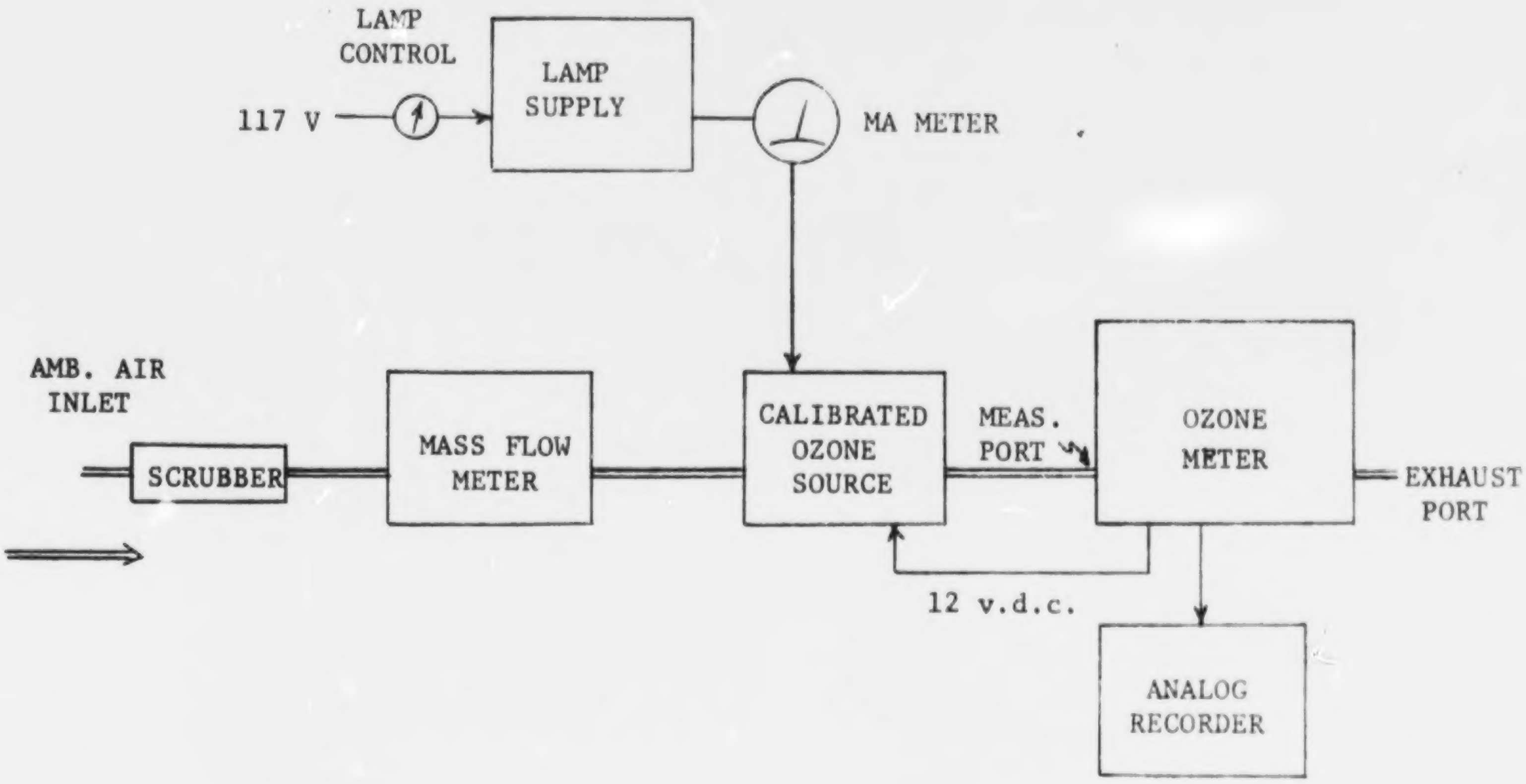

LAMP CONTROL
117 V
LAMP SUPPLY
MA METER
AMB. AIR INLET
SCRUBBER
MASS FLOW METER
CALIBRATED OZONE SOURCE
MEAS. PORT
OZONE METER
EXHAUST PORT
12 v.d.c.
ANALOG RECORDER

FIGURE 24. CALIBRATION UNIT, IN SITU CALIBRATION

4.5 Timing and Control Unit

The timing and control unit provides selectable timing cycles for the sample air and calibrate air solenoids and the calibrate lamp shutter. A circuit diagram for the timing and control unit is shown in Fig. 25. There are three automatic modes and three manual modes of operation which are push button selectable from the front panel of the instrument. The manual modes are as follows:

CONT RUN - continuous operation in the measure mode; i.e., the sample air solenoid open and the calibration lamp shutter closed.

CONT CAL - continuous operation in the calibrate mode; i.e., the calibrate air solenoid open and the calibrate lamp shutter open.

EXT - remote switch may be used to select CONT RUN or CONT CAL mode.

The three automatic modes of operation are described in Fig. 26. These are essentially as follows:

SAMP - 4 min cycle consisting of one min measure, one min purge, one min calibrate, and one min purge.

6 HR - 6 hour cycle, operating in the RUN mode continuously except for the 15 min CALIB mode at the end of each cycle.

12 HR - 12 hour cycle (otherwise identical to 6 hour cycle).

The indicated calibration times for the automatic modes (i.e., 15 min) are those initially set into each unit; these are adjustable and may be set for any range from 2% to 98% of the total cycle time. Cycle time may be varied by changing rack assemblies available from the timer manufacturer (see parts list). The timer adjustment procedure is given in Appendix C.6.

A 12 VDC power supply, located on the main chassis supplies the voltages for the solenoids, calibrate lamp shutter relays and indicator lamps.

Event marker connections on the rear panel are connected to relay contacts which are closed coincident with the actuation of the calibrate air solenoid.

The AC voltage supply and buzzer for the PM tube shutter interlock circuit are located on the timer chassis. Details of the interlock circuit are given in Section 4.3.

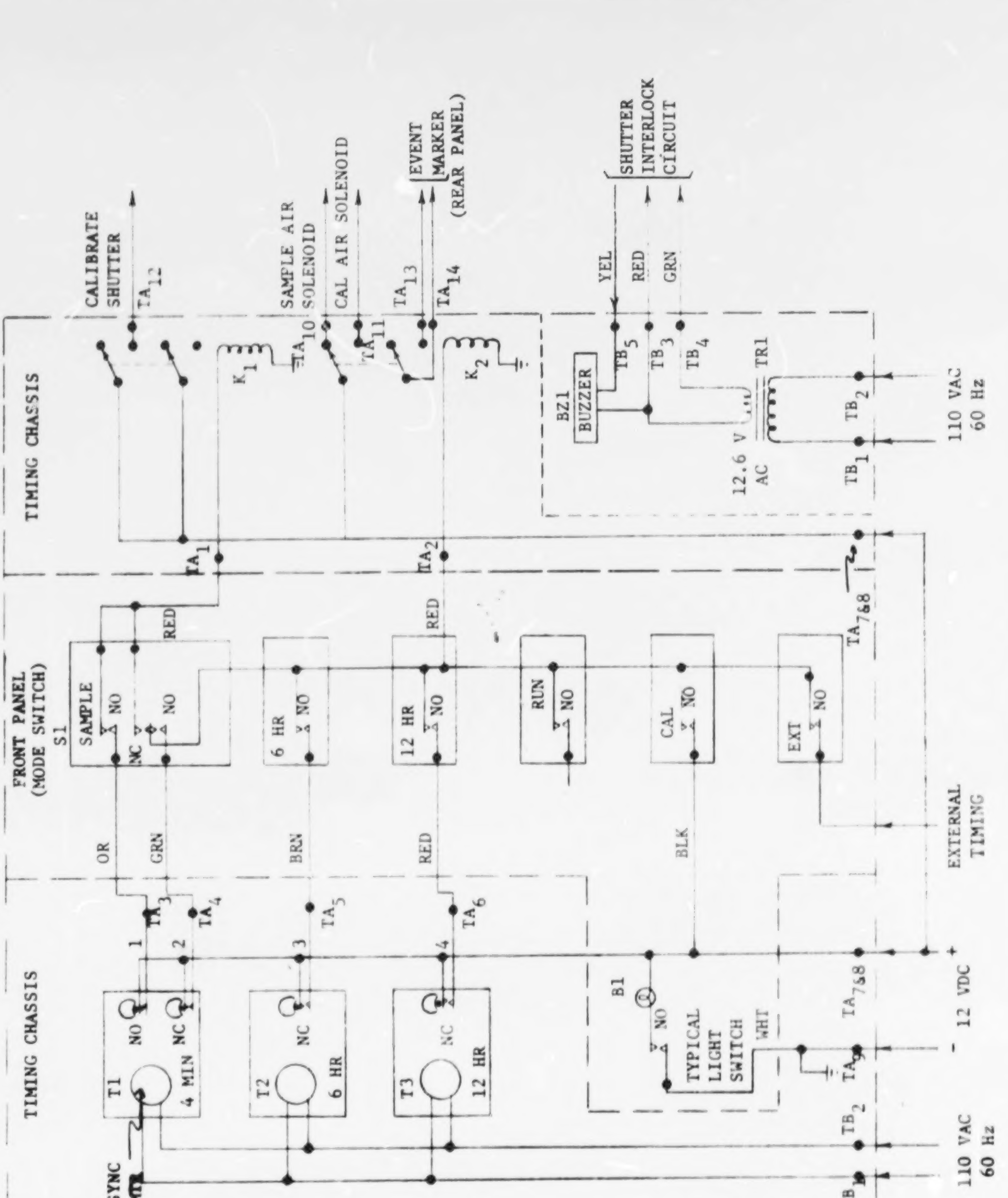

TIMING CHASSIS
CALIBRATE SHUTTER
TA_{12}
SAMPLE AIR SOLENOID
CAL AIR SOLENOID
TA_{10}
TA_{11}
TA_{13}
TA_{14}
EVENT MARKER (REAR PANEL)
K_1
K_2
SHUTTER INTERLOCK CIRCUIT
YEL
RED
GRN
BZ1
BUZZER
TB_5
TB_3
TB_4
TR1
12.6 V AC
TB_1
TB_2
110 VAC 60 Hz
TA_1
TA_2
$TA_{7\&8}$
FRONT PANEL (MODE SWITCH) S1
SAMPLE
NO
NC
NO
RED
6 HR
NO
12 HR
NO
RED
RUN
NO
CAL
NO
EXT
NO
EXTERNAL TIMING
OR
GRN
BRN
RED
BLK
TIMING CHASSIS
TA_3
TA_4
TA_5
TA_6
1
2
3
4
T1
NO
NC
4 MIN
T2
NC
6 HR
T3
NC
12 HR
SYNC MTR
B1
NO
TYPICAL LIGHT SWITCH
WHT
$TA_{7\&8}$
TA_9
+ 12 VDC -
TB_2
TB_1
110 VAC 60 Hz

FIGURE 25. TIMING AND CONTROL CIRCUIT DIAGRAM

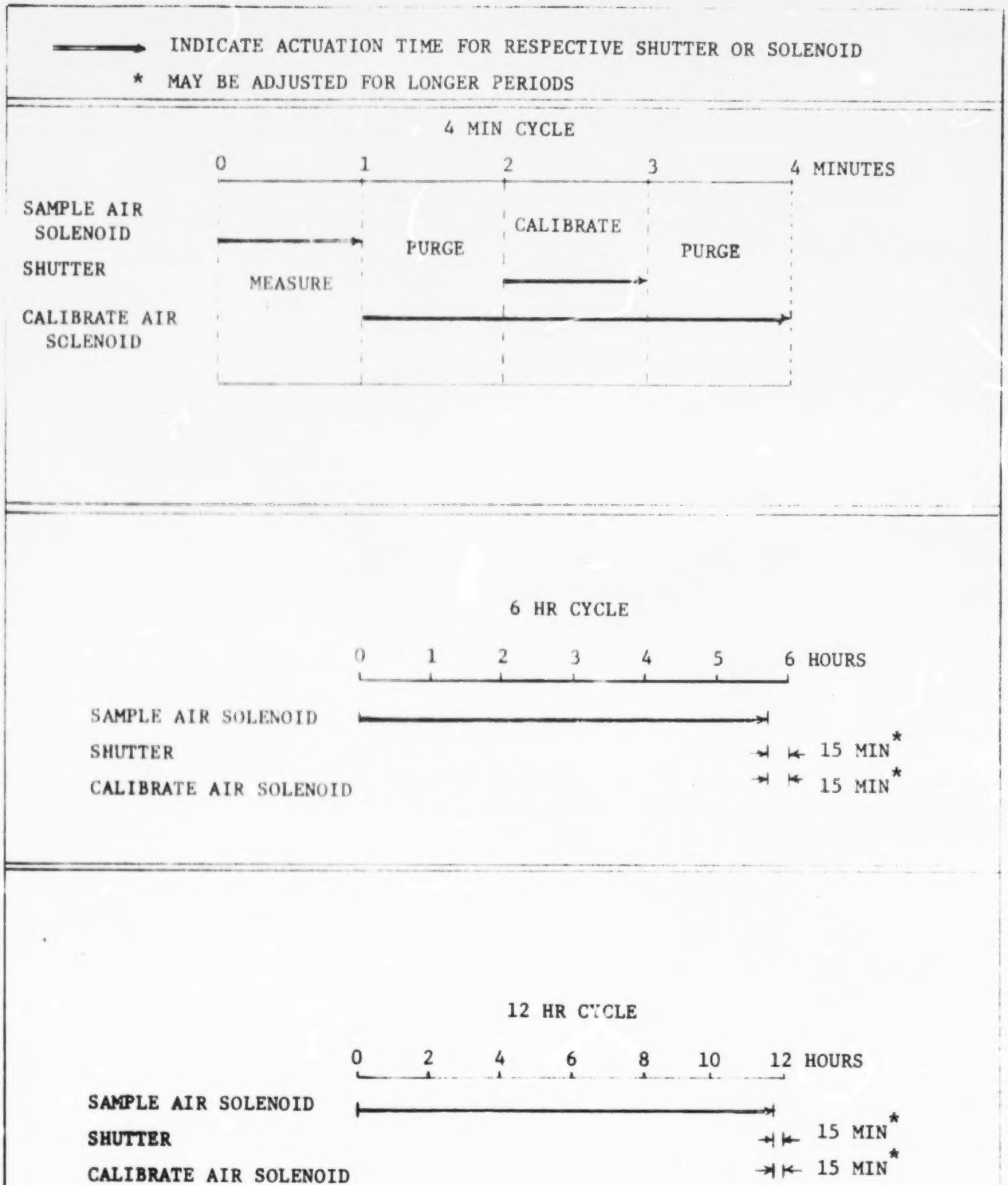

INDICATE ACTUATION TIME FOR RESPECTIVE SHUTTER OR SOLENOID
* MAY BE ADJUSTED FOR LONGER PERIODS
4 MIN CYCLE
0
1
2
3
4 MINUTES
SAMPLE AIR SOLENOID
SHUTTER
CALIBRATE AIR SOLENOID
MEASURE
PURGE
CALIBRATE
PURGE
6 HR CYCLE
0
1
2
3
4
5
6 HOURS
SAMPLE AIR SOLENOID
SHUTTER
CALIBRATE AIR SOLENOID
15 MIN*
15 MIN*
12 HR CYCLE
0
2
4
6
8
10
12 HOURS
SAMPLE AIR SOLENOID
SHUTTER
CALIBRATE AIR SOLENOID
15 MIN*
15 MIN*

FIGURE 26. AUTOMATIC TIMING CYCLES

4.6 Log/Linear Amplifier

4.6.1 Description -- The amplifier performs the function of raising the photomultiplier tube anode current from the lowest expected values, on the order of 10^{-9} amps, to the desired 0-1 volt output. A block diagram of the amplifier subsystem is given in Fig. 27. The amplifier is basically a calibrated current meter incorporating a three-decade logarithmic range and five linear ranges. In addition, certain other desirable functions are provided such as an output attenuator and time constant control. A detailed circuit diagram is given in Fig. 28. A summary of the amplifier characteristics is given below:

Sensitivity: Linear - 10^{-9} amps, FS
10^{-8} amps, FS
10^{-7} amps, FS
10^{-6} amps, FS
10^{-5} amps, FS

Log - 10^{-9} to 10^{-6} amps, (zero to FS values)

Input Impedance - 10^{7} ohm
(effective load impedance for PM tube)

Noise - 10 μV p-p, .01 to 1 Hz

Output - 0-1 volt, recorder output jack
(5 mA max current)

Drift - Linear - 10 μV/°C (equiv. to input offset)

Log - < 0.5% for 60 hours
(for worst-case condition)

Time Constant - Normal
1 sec, 10 sec, 40 sec

Dark Current Offset - 0 to 10^{-8} amps

The input current (PM tube anode current) is passed through a 10^{7} ohm voltage divider. This voltage divider not only provides a known fixed resistance but on the two least sensitive ranges it provides voltage division of 10 or 100 to prevent overload of the input stages of the amplifier.

The voltage drop across the divider is then sensed by a varactor bridge operational amplifier. This particular unit, the Analog Devices 311J, was selected for its low bias current (10^{-14} amp), low bias current drift (10^{-15} amp/°C) and high input impedance (10^{14} ohm). This amplifier boosts the lower level signals to a usable level as well as isolating the voltage divider from any loading effects.

When the range switch is in the logarithmic position, the output of the varactor bridge amplifier is fed into an OEI 2245 logarithmic amplifier instead of directly to the output amplifier. A variable voltage divider drops the output of the log amp down to 0.33 V/decade. An Analog Devices Model 183K differential amplifier is used to shift the level of the signal so that 10^{-9} amps (10 mV), input corresponds to zero output. The output of the differential amplifier is then fed into the output amplifier (another AD-183K) through the log position on the last section of the range switch.

The log scale calibration curve is shown in Fig. 29, and the linear scales are shown in Fig. 30. The signal is fed into the output amplifier through a three-position attenuator. This configuration gives a gain of 1, ½ or ¼ for full scale multiplying factors of 1, 2, or 4 respectively. Capacitors are placed across the feedback resistor in the output amplifier to provide filtering to reduce high frequency noise and smooth the output. A four-position switch selects the proper capacitor for a time constant of normal, 1, 10, or 40 seconds. The output is brought out of the amplifier box through two BNC connectors connected in parallel. The front panel meter is connected to one and a rear panel recorder output jack is connected to the other.

Dark current offset or base line adjustment is provided by a bucking voltage fed into the top of the 10^7 ohm PM tube anode load. This is controlled by a 10 turn potentiometer and is adjusted for zero offset at zero reading on the dial, and provides linear offset up to 10^{-8} amps at a dial setting of 100. This is shown in Fig. 31.

The unit is completely self contained. An Analog Devices 100 mA ± 15 volt power supply allows the unit to be operated directly from 115 VAC. It is enclosed in an aluminum box with removable side plates and switch shafts long enough to reach through the front panel.

Standard maintenance and calibration procedures for the amplifier are given in Appendix C.7.

4.6.2 Test Procedures and Results -- Since this unit is to be run over extended periods of time it is necessary that the unit be very stable in both zero base line drift and gain accuracy drift. In addition to providing amplification, it would be desirable to build filtering circuits into the amplifier which remove only the noise on the signal without attenuating the DC component. A description of the tests performed and the results are presented in the following paragraphs.

Extensive tests were performed to determine the performance of all units individually. Among these were tests for gain accuracy and linearity, stability, and noise. In addition to these tests a single unit (EU-414-02) was tested for response to step functions and pulses and frequency response.

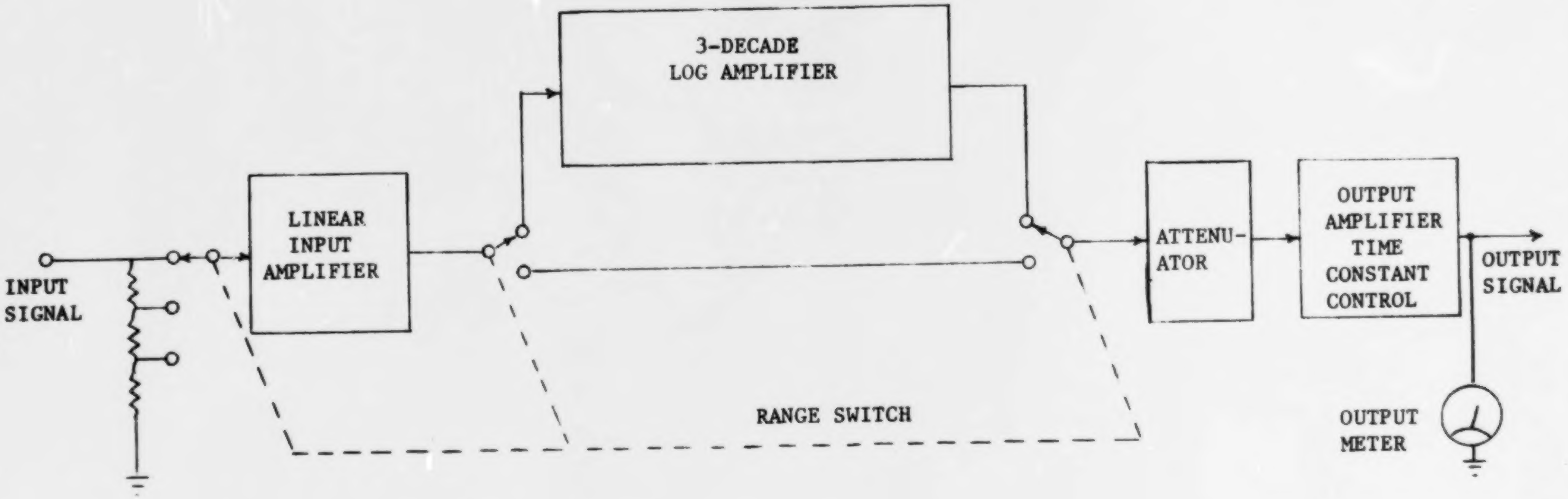

INPUT SIGNAL
LINEAR INPUT AMPLIFIER
3-DECADE LOG AMPLIFIER
RANGE SWITCH
ATTENU-ATOR
OUTPUT AMPLIFIER TIME CONSTANT CONTROL
OUTPUT SIGNAL
OUTPUT METER

FIGURE 27. FUNCTIONAL DIAGRAM OF AMPLIFIER

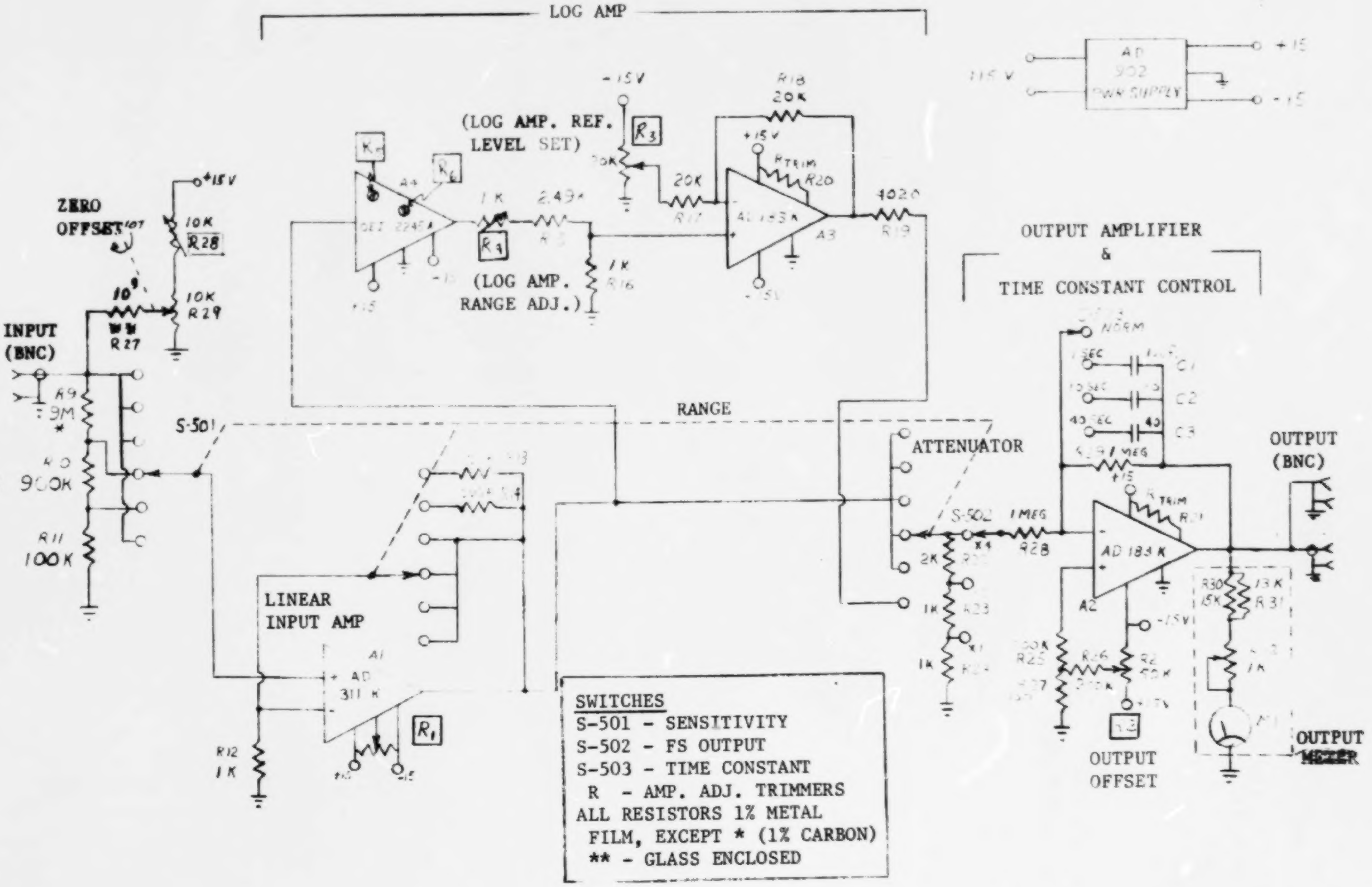

LOG AMP
(LOG AMP. REF. LEVEL SET)
(LOG AMP. RANGE ADJ.)
R18 20K
R17 20K
R16 1K
R19
R20
A3
A4
R3
R4
R6
-15V
+15V
2.49K
1K
ZERO OFFSET
10K R28
10K R29
R27
+15V
INPUT (BNC)
R9 9M *
R10 900K
R11 100K
S-501
RANGE
LINEAR INPUT AMP
A1
AD 311 K
R1
R12 1K
ATTENUATOR
S-502
1MEG R28
2K
1K R23
1K
OUTPUT AMPLIFIER & TIME CONSTANT CONTROL
NORM
1 SEC
10 SEC
40 SEC
C1
C2
C3
A2
AD 183 K
-15V
R25
R26
R27
OUTPUT OFFSET
R30 15K
13K R31
1K
OUTPUT (BNC)
OUTPUT METER
AD 902 PWR SUPPLY
115 V
+15
-15
SWITCHES
S-501 - SENSITIVITY
S-502 - FS OUTPUT
S-503 - TIME CONSTANT
R - AMP. ADJ. TRIMMERS
ALL RESISTORS 1% METAL FILM, EXCEPT * (1% CARBON)
** - GLASS ENCLOSED

FIGURE 28. PHOTOMULTIPLIER TUBE LOG/LINEAR AMPLIFIER

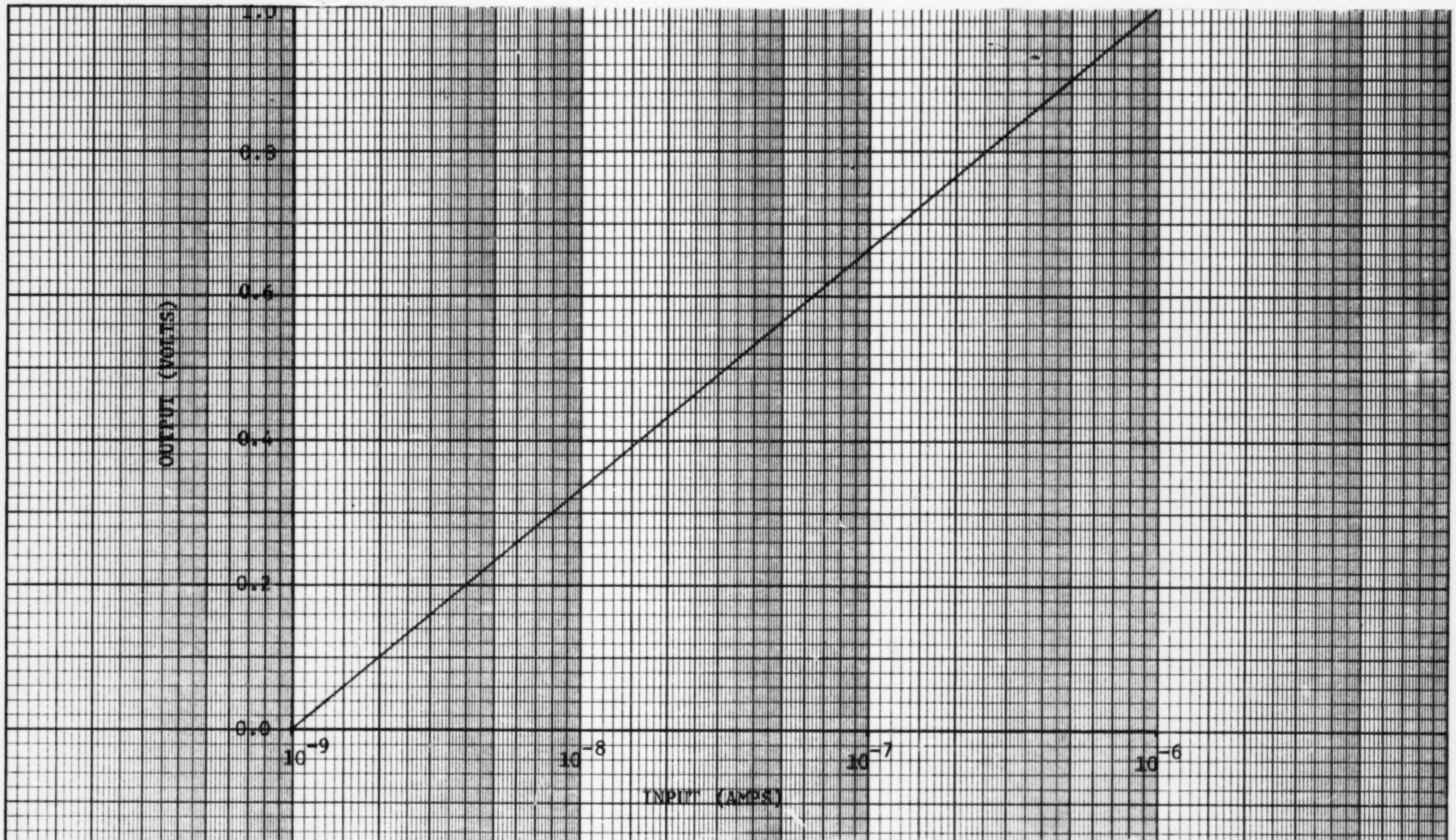


FIGURE 29. AMPLIFIER OUTPUT VOLTAGE VERSUS INPUT CURRENT FOR LOG RANGE

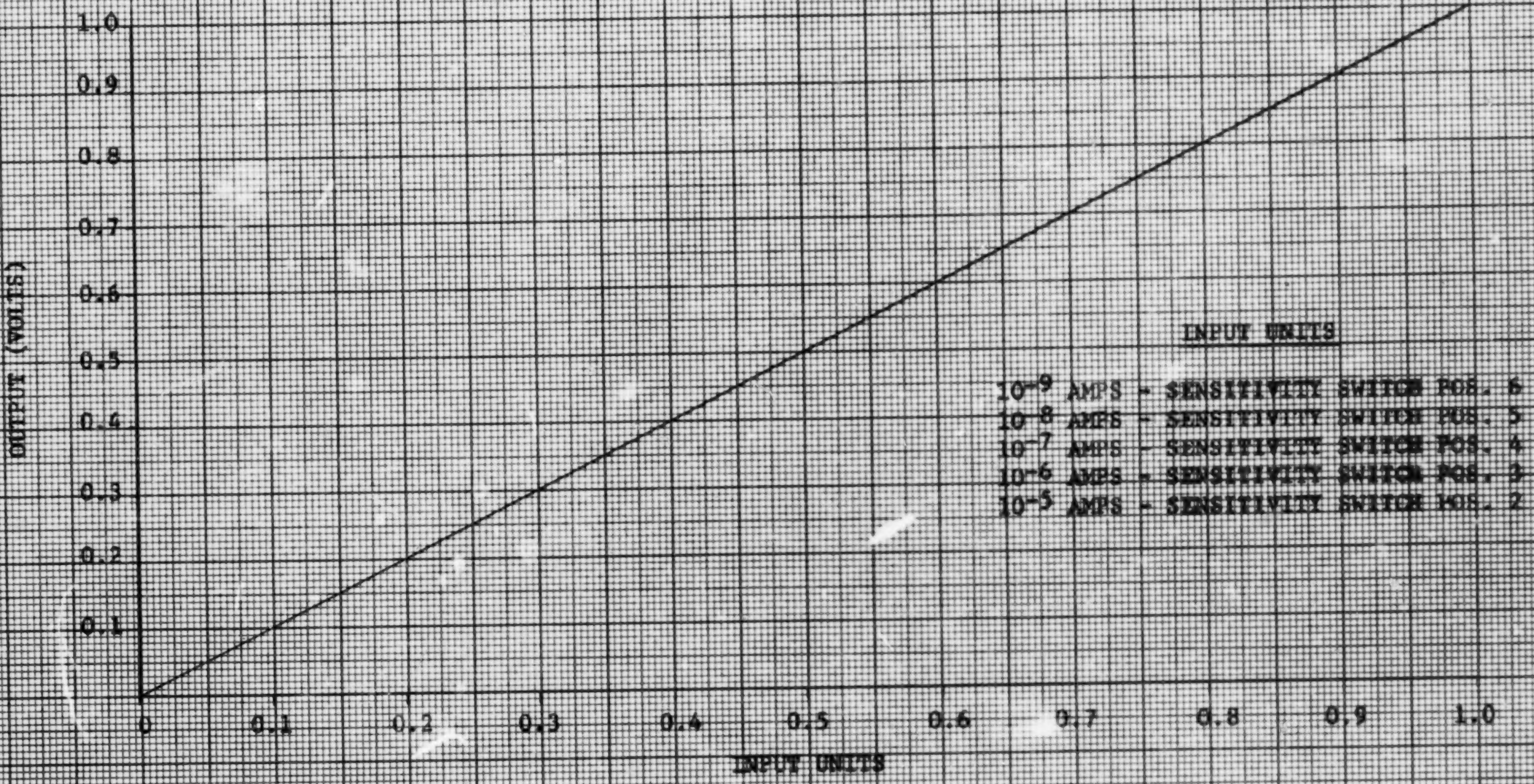


FIGURE 30. AMPLIFIER OUTPUT VOLTAGE VERSUS INPUT CURRENT FOR LINEAR RANGES

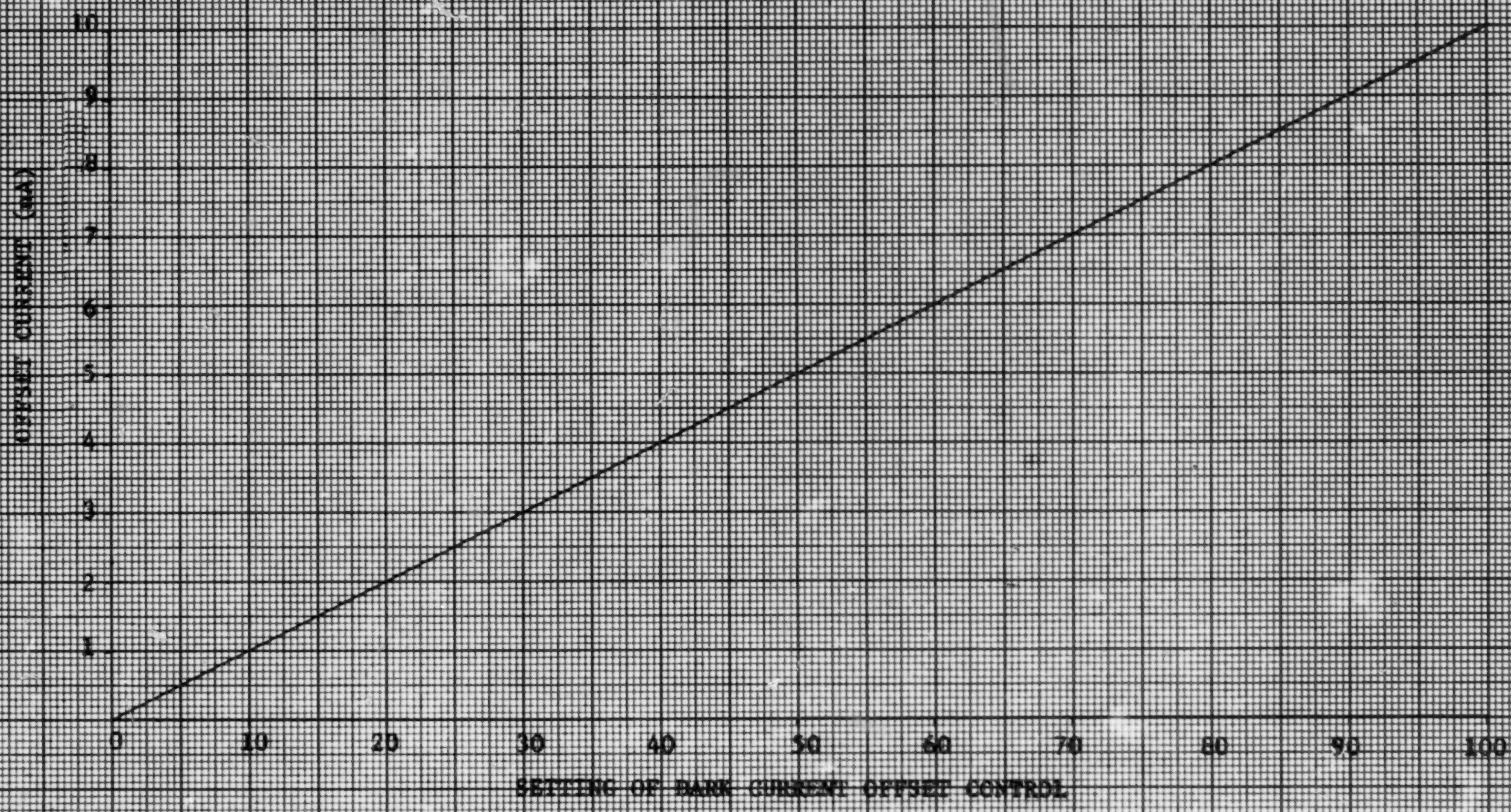


FIGURE 31, DARK CURRENT OFFSET

To test the gain accuracy, the amplifier was connected to a stable power supply and an accurate digital voltmeter as shown in Fig. 32. The input voltage was varied from 1 mV to 20 V in 3 steps per decade in the linear ranges and 3 mV to 10 V in 2 steps per decade in the log range. This yields at least 7 data points per range switch position. The maximum deviation from the desired linear gain curve is expressed as max percent error as given for each unit in Table 8.

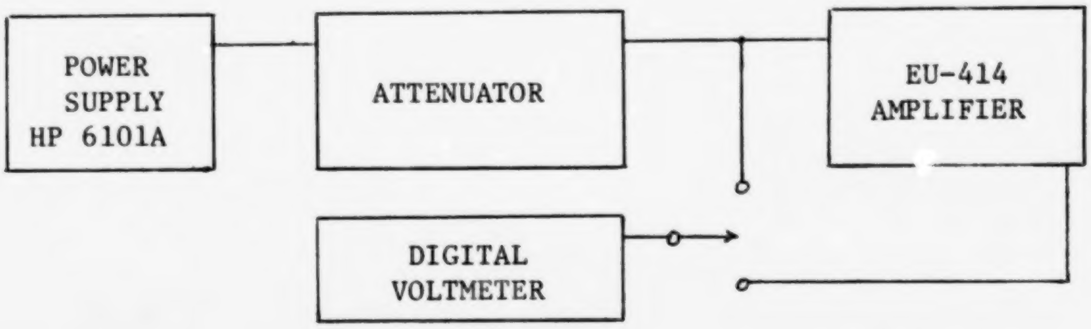

POWER SUPPLY HP 6101A
ATTENUATOR
EU-414 AMPLIFIER
DIGITAL VOLTMETER

FIGURE 32 . GAIN TEST

Table 8

GAIN ACCURACY

Unit Number	Max % Error
1	0.9
2	0.9
3	1.0
4	0.7
5	0.8
6	0.7

The stability of the amplifier was checked in both the linear and logarithmic modes. For the linear case the input was left unconnected and the gain set on maximum (10^{-9} amps, which is equivalent to 10 mV full scale). The output was then monitored on a HP 680 strip chart recorder for at least 12 hours and in some cases up to 72 hours.

The stability check for the logarithmic amplifier was somewhat different. Since the log amp is referenced such that zero output corresponds to 10 mV or 1 nA input, leaving the input open would drive the amplifier off scale in the negative direction. Also, if 10 V were applied for full scale output, the incremental gain of the amplifier would be so low that any causes of drift might be unobservable. For these reasons the input was connected to a 10 mV source, which is the highest-gain on-scale operating point of the amplifier in the log mode. The output was connected to a HP 680 strip chart recorder and observed for periods of 12 to 72 hours.

In all of the drift data taken in which the periods ranged from 6 hrs to 60 hrs, the output never drifted more than 1 percent full scale, or 10 mV out of the 1 V FS output, after a 1 hr warm-up period. From a cold start in the log mode, one unit showed a drift of 40 mV in the first hour and a half and then settled down to less than 10 mV for the remainder of the 24 hr run.

The frequency response was measured in a conventional manner, a low frequency signal generator was hooked to the input and the output of the amplifier measured for various input frequencies. Only the three highest gain positions were used since below this the gain is determined by voltage division in the input divider and the frequency response curve is the same as that of the 10^{-7} amp FS range. The above measurements were carried out with the time constant switch in the normal position. The results of these tests for gains of 1, 10 and 100 are shown in Fig. 33.

The effectiveness of the filters were checked by applying step functions to the input and recording the output either on a scope with camera or on a strip chart recorder. These are shown in the scope photographs in Figs. 34, 35, and 36 for time constant settings of normal, 1 sec, and 10 sec, respectively. The upper trace is the output response, the input waveform is shown in the lower trace. The horizontal sweep and vertical gain are identical in all three illustrations; the 40 sec time constant was checked on a strip chart recorder but is not shown.

A noise test on the amplifier was performed. The amplifier input was left open and the gain turned to maximum. The output was then connected to an oscilloscope and photographed. Likewise the noise was photographed in the log position while the input was connected to 10 mV source for one case and left open for another. The p-p noise measured with no filter for both the linear and log modes was approximately 10 μV

It should be noted that there is 60 Hz ripple present in the output in the log mode with zero input; this is due to the extremely high gain of the log amp for this condition. This waveform should be reasonably symmetrical or the input balance control on the log amp should be adjusted (see calibration procedure).

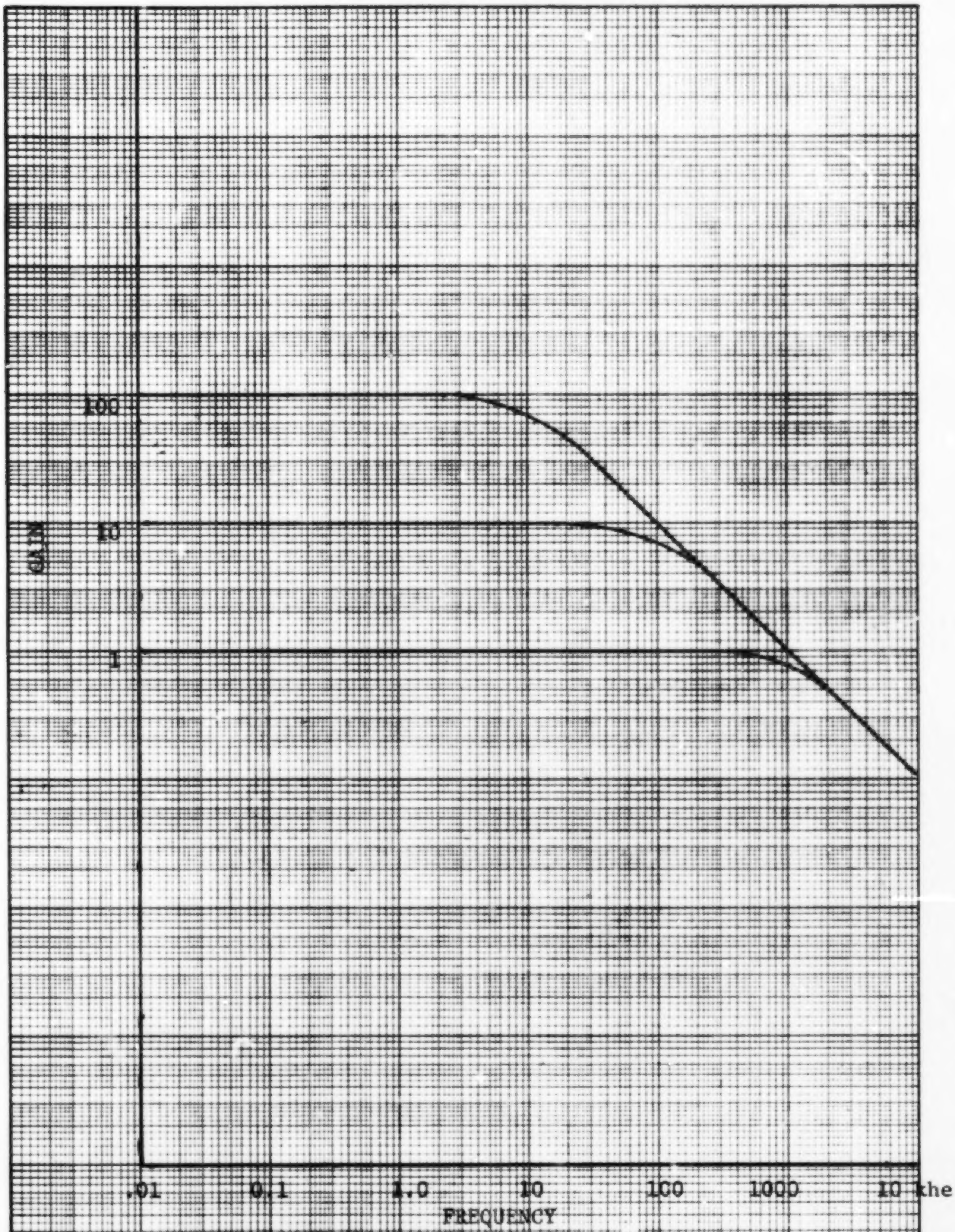


FIGURE 33. FREQUENCY RESPONSE OF EU-414-02 AMPLIFIER FOR VARIOUS GAINS OF INPUT AMPLIFIER

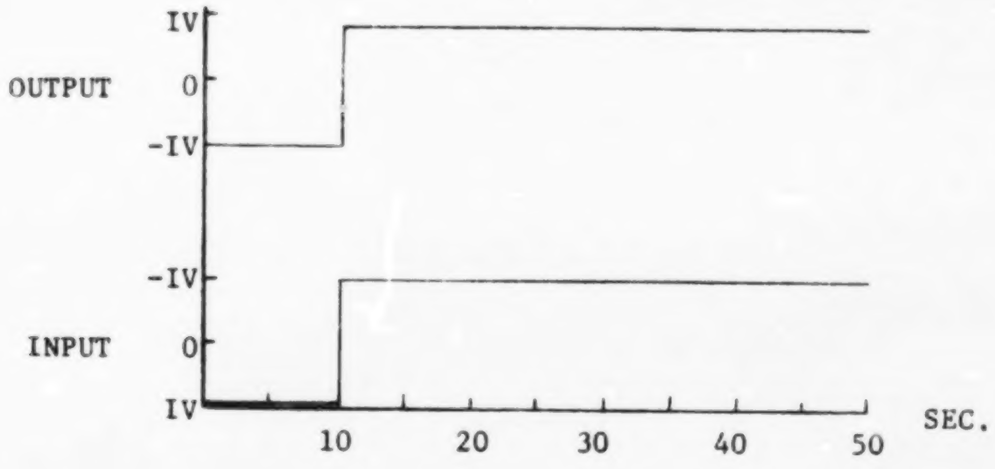


FIGURE 34 τ = NORMAL

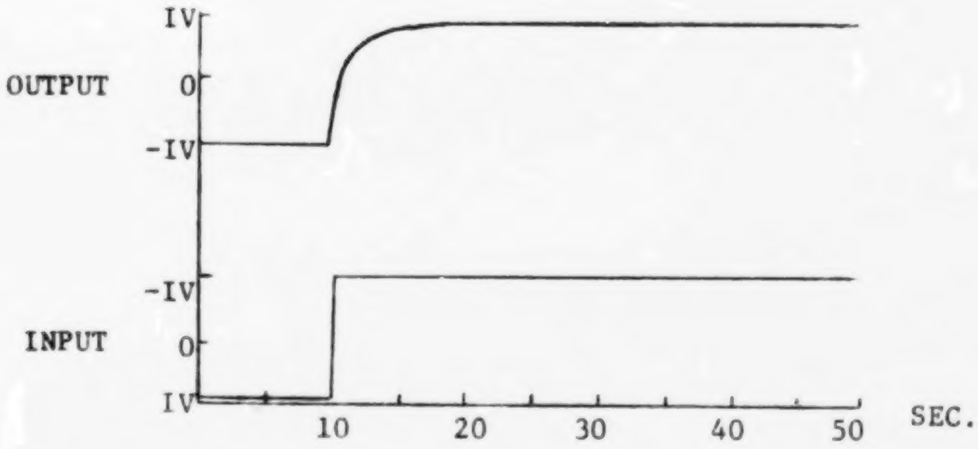


FIGURE 35 τ = 1 SECOND

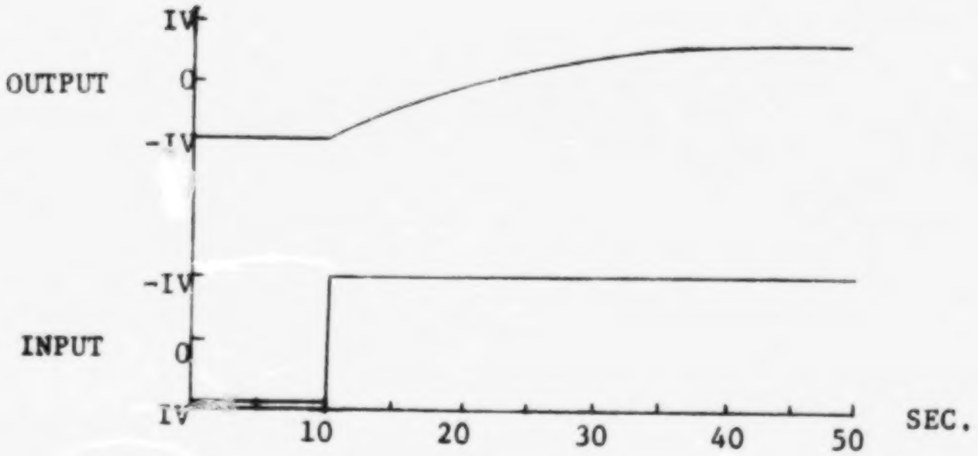


FIGURE 36 τ = 10 SECONDS

RESPONSE OF AMPLIFIER TO STEP FUNCTION INPUT
AMPLIFIER-10^{-7} AMP (IV) FULL SCALE, OUTPUT SENSITIVITY XI

5.0 CONCLUSIONS AND RECOMMENDATIONS

The ozone meter was designed as a laboratory instrument for the purpose of evaluating the chemiluminescent sensor technique. Therefore, the meter is considerably more sophisticated in design than would be necessary for a meter that is designed as a production unit. This versatility in design provides for a wide lattitude of test conditions thereby permitting one to determine the effect of each parameter (such as flow rate, temperature, line voltage, etc.) and their interdependencies.

During the process of design, fabrication and testing, several things have been noted which need to be investigated further, or a design improvement which might be implemented in later models.

One need is for a standard light emission source to calibrate/establish the response of the photomultiplier tube. It would be advisable to use a light source which emitted only in the spectrum of interest or else use filters. At the present time the PM tubes are roughly compared by interchanging them in the same unit. Present work in evaluation of discs must assume, to a large extent, that there is no significant change in the PM tube characteristics over the period of the tests. To a large extent, this is a safe assumption. It is very desirable to be able to establish a fixed reference so that evaluations over time may be compared with a known degree of confidence. One possibility for the light emitter is a radioactive source, Model 1H1C Sr-90 Cerenkov Generator, supplied by Minnesota Mining and Mfg. Co. The usefulness of this device for this purpose needs to be evaluated.

Another area of further investigation would be in the determination of the optimum size PM tube and the possible use of an optical system to concentrate the light emitted from the disc onto the photomultiplier tube cathode. The use of smaller diameter PM tubes results, in general, in lower values of dark current and hence possibly improved sensitivity. The cost of an optical system would be a trade-off which needs to be investigated.

A closely related investigation would have to do with the use of a solid state detector in place of the PM tube. The trade-off here would be in sensitivity for a sharp reduction in size, weight and cost.

Where changing manifold pressures are expected it would be advisable to consider a redesign of the dilution system to preclude the error caused by changing source pressure. This may be solved to a large extent by adding a separate pump to the dilution line or reducing the dilution flow to zero. The method of correction would depend on considerations such as cost of the extra pump or the effect of shutting off the dilution flow.

Future models of this instrument could probably be reduced in size and weight by a factor of two without too much difficulty.

6.0 REFERENCES

[1] J. R. Smith, H. G. Richter, and L. A. Ripperton, "Chemiluminescent Ozone Measurement Program (Urban Atmospheres)," Final Report, December 1967, National Center for Air Pollution Control, Contract PH 27-68-26.

[2] A. J. Bernanose and M. G. Réné, "Oxyluminescence of a Few Fluorescent Compounds of Ozone," in Ozone Chemistry and Technology, American Chemical Society, 1959.

[3] V. H. Regener, "Measurement of Atmospheric Ozone with the Chemiluminescent Method," J. Geophys. Res., 69, 3795 (1964).

[4] V. H. Regener, "On a Sensitive Method for the Recording of Atmospheric Ozone," J. Geophys. Res., 65, 3975-3977 (1960).

[5] V. H. Regener, et al., "The Preparation of a Chemiluminescent Substance for the Measurement of Atmospheric Ozone," AD 632 562, March 31, 1966.

[6] E. R. Stephens, E. F. Carley, and O. C. Taylor, "Photochemical Reaction Products in Air Pollution," Intern. J. Air Water Pollution, 4, 79 (1961).

APPENDICES

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APPENDIX A

CALIBRATION PROCEDURES FOR THE CALIBRATION UNIT

Apparatus - The unit in test was placed in line with an ozone-moisture trap of Drierite and No. 40 mesh charcoal, a mass flowmeter, two 25 ml graduated all glass inpingers (open end nozzle type), an air flow control valve and air pump (refer to Fig. 37). Quartz tube to impinger connection was accomplished by means of a teflon reducing union, glass tubing and a ground glass joint, slightly lubricated with Kel-F No. 90 stopcock grease. A 12 VDC power supply was used to activate the internal shutter and the UV lamp current was adjusted by means of an autotransformer and a Pen Ray 10 mA transformer. All tests were timed with an electronic timer and AC power was regulated at 117 volts.

Air flow was metered with a Hastings mass flowmeter (a thermoelectric type sensor) with a range of 0 to 300 standard ml/min, readable to 1.5 ml/min and stable within 2% to 250psia.

Reagents - The absorbing reagent was prepared with reagent grade chemicals - 13.61g potassium dihydrogen phosphate, 14.2g of anhydrous disodium hydrogen phosphate and 10.0g of potassium iodide, diluted to 1.0 liter with distilled water which had been passed through two ion exchange columns and a millipore filter. Prior to initial use, each new batch of absorbing reagent was aged for 24 hrs. in the dark and at room temperature.

Standard iodine solution, 0.05N, was prepared by carefully weighing 16.0g of potassium iodide and 3.173g of iodine and diluted to exactly 0.5 liter.

Procedure - Exactly 10 ml of the absorbing reagent was pipetted into each of two tandem impingers, carefully shielding the solution from light whenever possible.

Ambient air was aspirated through the assembled train for sampling periods of 15 to 30 minutes, at flow rates between 50 to 300 ml/min. Immediately following sampling, the exposed absorbing solution was transferred first to a graduated cylinder, then to a 1 inch diameter colorimeter cuvette. At the lower flow rates (i.e., less than 300 ml/min), no appreciable evaporation was observed in either impinger.

Analysis - Absorbance was determined within 10 to 15 minutes after sampling, with a Bausch and Lomb Spectronic 20 Spectrophotometer, at 352 nm and with unexposed absorbing reagent as the reference.

Standardization was checked each day during the test, with an 0.0025N iodine standard solution prepared by pipetting 5 ml of the 0.05N standard stock solution into a volumetric flask and diluting to 100 ml with absorbing reagent. A series of 0.2, 0.4, 0.6, and 0.9 ml portions of the diluted standard iodine were pipetted into volumetric flasks and diluted to 25 ml with absorbing reagent and the absorbance of this known series was determined at 352 nm.

Calculations - Absorbance and calculated normality of the standard iodine solution was plotted (refer to Fig. 38), and the standardization factor, M, was determined from the normality of the standard solution at absorbance 1.0.

O_3 (ppm) = Sample absorbance x M/V (Ref. A-1)

where: M (standardizations factor) = $1.224 \times 10^5 I$
I = Intercept at absorbance 1.0 and
V = Volume of sample in liters

The above calculations were executed, assuming no deviation from the standard conditions of 760 mm of mercury and 25°c, and the air sample volume was used directly as recorded.

Then: Volume = 24.47 liters
$1\mu\ I_2 = 24.47\ \mu l\ O_3$ and
10 ml 1N iodine = $5 \times 10^3\ \mu$mole $I_2 = 1.224 \times 10\ \mu l\ O_3$

Procedure efficiency - Varying the sampling time, not exceeding a maximum of 30 minutes or a minimum of 15 minutes and obtaining the absorbance reading at intervals of 10 to 15 minutes after sampling, the error observed between consecutive samples was negligible. Variations did occur among successive batches of absorbing reagent, which gave only 93% reproducibility.

Ref. A-1 Saltzman, B. E., Determination of Oxidants (including Ozone): Neutral Buffered-Potassium Iodide Method, Public Health Service Publication No. 999-AP-11.

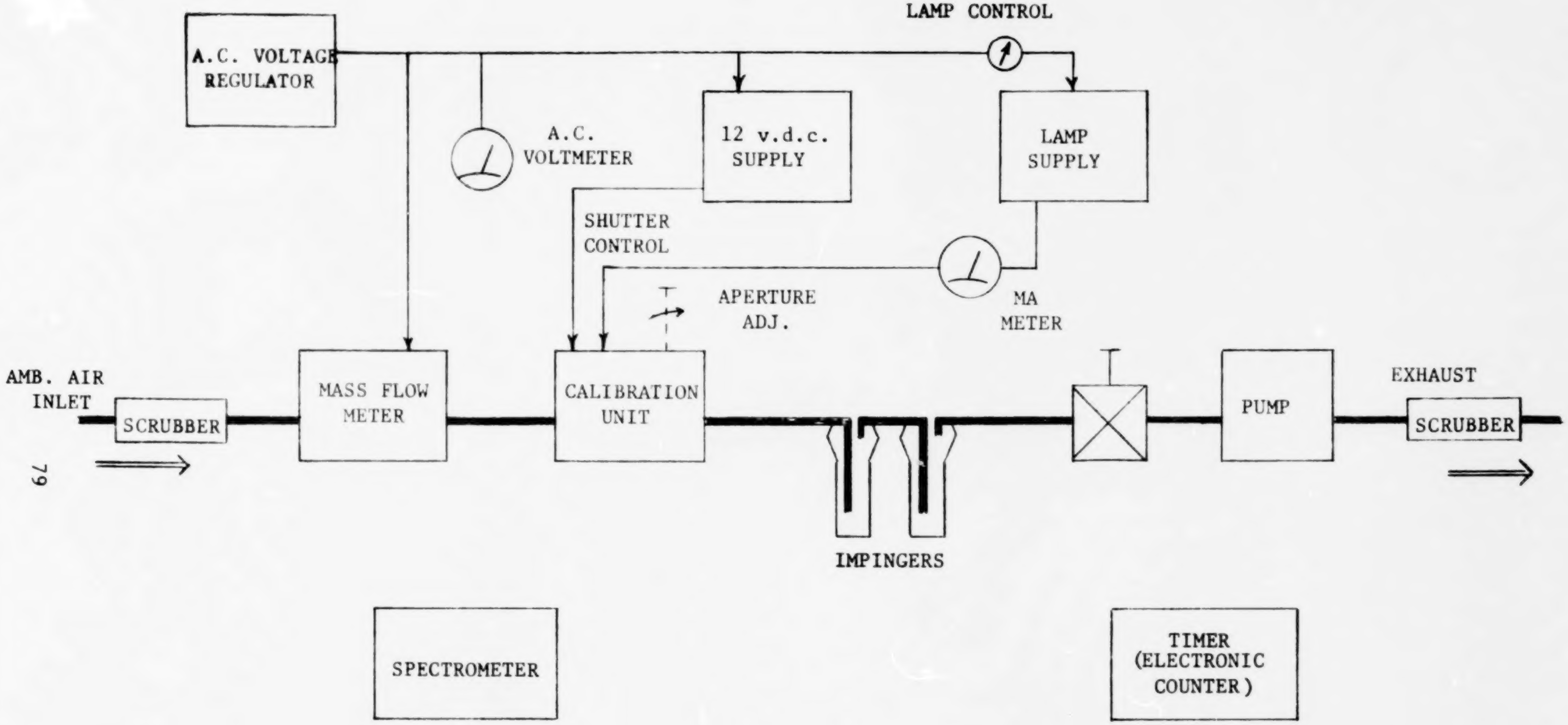

A.C. VOLTAGE REGULATOR
LAMP CONTROL
A.C. VOLTMETER
12 v.d.c. SUPPLY
LAMP SUPPLY
SHUTTER CONTROL
APERTURE ADJ.
MA METER
AMB. AIR INLET
SCRUBBER
MASS FLOW METER
CALIBRATION UNIT
IMPINGERS
PUMP
EXHAUST
SCRUBBER
SPECTROMETER
TIMER (ELECTRONIC COUNTER)

FIGURE 37. CALIBRATION UNIT, CALIBRATION FUNCTIONAL DIAGRAM

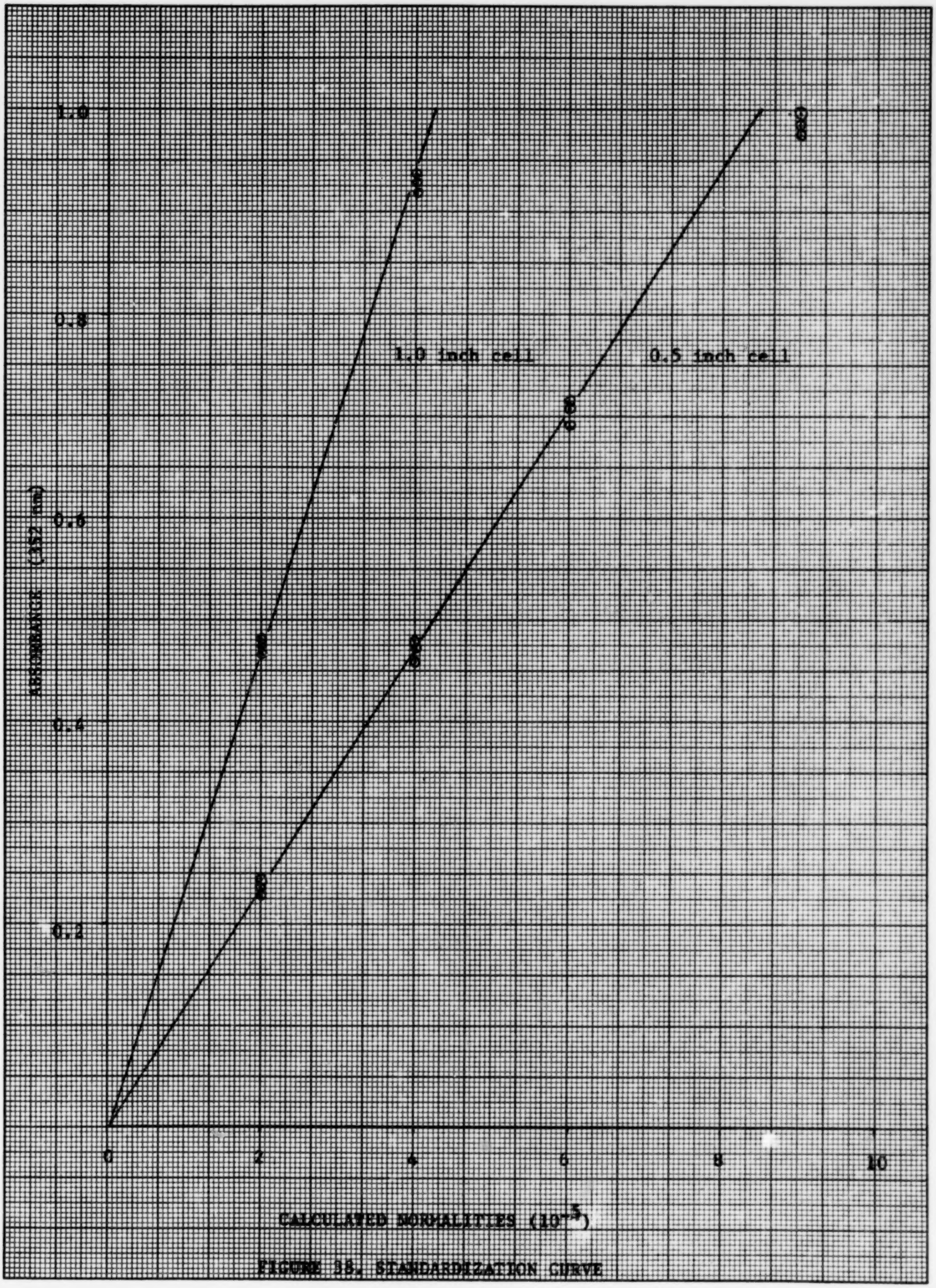


FIGURE 38. STANDARDIZATION CURVE

APPENDIX B

INSTALLATION AND OPERATION

B.1 Preliminary Set-up Procedure

(1) Access to Main Chassis

(a) Remove screws from front panel.

(b) Check for freedom of movement of air inlet line, signal cable, and power cable at rear of unit, or disconnect as appropriate.

(c) Slide chassis out until it stops.

NOTE: A safety chain restrains the chassis from extending beyond the first stop. This should not be removed unless chassis is to be removed completely from cabinet.

(2) Install Photomultiplier Tube

(a) Install the PM tube in the PM tube housing and mount on detector unit.

NOTE: Care should be taken not to expose the PM tube to strong light; excessive exposure requires approximately 24-48 hours for dark current to decay to normal value.

(3) Attach the HV and signal coax cables to the PM tube housing.

(4) Remove shunt wire from output meter terminals. (This shunt wire is a precautionary measure taken in shipping to prevent damage).

(5) Visually Inspect unit for any obvious damage.

(6) Check condition of drying towers.

(7) Slide main chassis back in place.

NOTE: Open rear door and check tubing to drying towers to assure that tubing is not pinched.

(8) Install chemiluminescent disc (Appendix C.2).

CAUTION: The instrument is designed for normal operation with both front and rear panels in the closed condition. Opening either end will result in a temperature rise in certain components. Complete removal of chassis is satisfactory providing ventilation below chassis is provided.

B.2 Turn-On Procedure

(1) Close shutter - full closure indicated by AMBER Lamp.

(2) Set SENSITIVITY to 5.

(3) Set FS OUTPUT to 1.

(4) Set TIME CONSTANT to NORMAL.

(5) Adjust HV to recommended value for gain of 200 (see specification sheet).

(6) REPLACE HV Power Supply Cover.

(7) Turn AC POWER switch to ON.

> NOTE: Initial operation procedures should include purging of the air intake lines with high levels of ozone to destroy contaminants.

B.3 Operational Adjustments/Checks

(1) Adjust LAMP CURRENT to 10 mA.

(2) Set DILUTION FLOW to 500 ml/min.
Set TOTAL FLOW to 600 ml/min.
(see spec sheet for proper flowmeter settings) (See Section C.3 for procedure)

(3) Check dark current - note value.

(4) Open shutter - full open indicated by RED Lamp.

(5) Switch to CAL mode - note value.

(6) Switch to desired operating mode.

(7) Set amplifier controls to desired range and time constant.

APPENDIX C

MAINTENANCE, CALIBRATION AND ADJUSTMENT PROCEDURES

C.1 Main Chassis Removal

(1) Remove screws from front panel.

(2) Open rear door and disconnect flexible hoses at C_1, C_2 and C_3. (See Fig. 12).

(3) Slide chassis out a few inches and disconnect the safety chain.

(4) Disconnect HV power supply AC cord and output cable, and fan power cord.

(5) Slide chassis out until safety catches on chassis slides stop movement. (The weight of the instrument should be supported by the operator.)

(6) Depress safety catches on slides and remove chassis from cabinet.

> NOTE: When operating unit out of cabinet, raise chassis 1"-2" off bench for increased component ventilation.

C.2 Disc Replacement

(1) Move shutter control to CLOSED position. CLOSED indicator light must be on.

(2) Open disc access door and lower disc holder by turning knob counterclockwise until holder stops. Lift holder enough to clear locating pins and pull unit forward. Be careful not to drag against top plate of unit.

(3) Replace old disc with new one making note of elapsed time.

(4) Place holder back in unit using two locating pins on bottom plate to correctly position holder. Be sure Neoprene outlet hose is not pinched behind holder, and O-ring is properly seated.

(5) Turn knob clockwise until holder is firmly seated. It may be necessary to use pliers to obtain a good seal. If possible, the system should be checked for leaks each time the disc is changed to avoid erroneous data.

C.3 Flow Rate Adjustment and Check

(1) The proper flow rates are as follows:

Inlet and exhaust	- 100 ml/min
Dilution	- 500 ml/min
Total	- 600 ml/min

(2) Adjustment of the air sampling rate is accomplished with the total air flow and fine dilution valves (front panel mounted) and the coarse dilution valve (located just behind the front panel). (See Fig. 13).

(3) Set the fine dilution valve wide open and the coarse dilution valve at approximately mid-range.

(4) With the internal flow control valve, adjust the total air flow to 600 ml/min (flow meter reading of 41).

(5) Adjust the dilution flow meter to 20 with the coarse dilution valve.

(6) Re-adjust the total air flow if necessary and carefully set the dilution flow to 500 ml per min. (see specs) with the fine dilution valve.

NOTE: A. Flow rates at the ambient air sampling port and the exhaust port should be checked periodically, either with a mass flow meter device or with a glass rotameter capable of measuring 100 ml/min with an accuracy of ± 2%. These tests will determine air leaks present in the system and will insure accurate air sampling. It is recommended that where an external flow meter is available that it be used to make final adjustments to the air flow.

B. A calibration curve for the flowmeter is shown in Fig. 39. This applies only to the total flowmeter since pressure drop in the system shifts the calibration curve for the dilution flowmeter.

C. The pressure at the manifold affects the flow rates, and therefore must be maintained at a constant value.

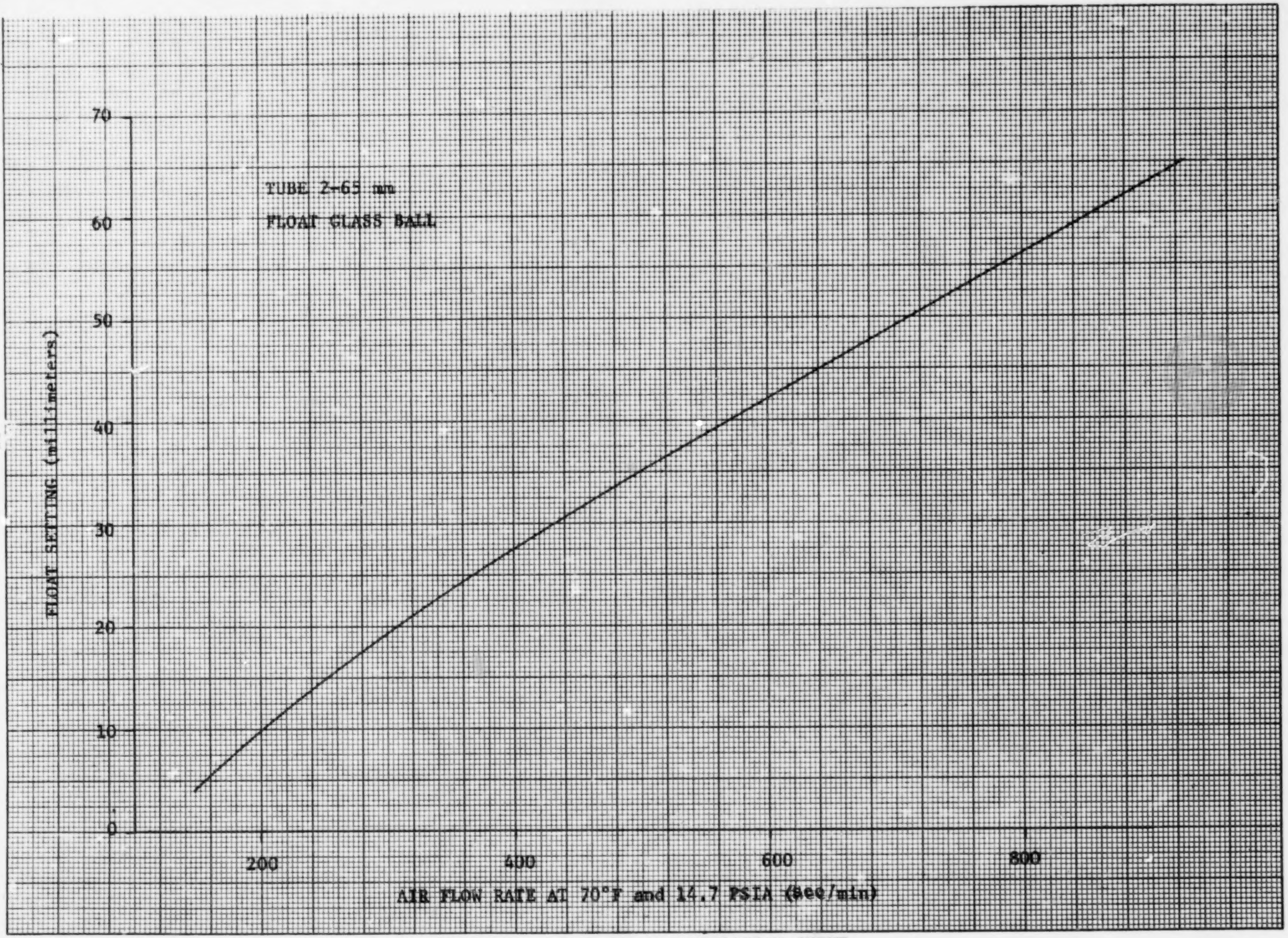


FIGURE 39. FLOWMETER CALIBRATION CURVE

C.4 Drying Tower/Maintenance

(1) The two drying towers located on the inside of the rear cabinet door should be inspected periodically and the material replaced or regenerated as required.

(2) The drying columns are filled with DRIERITE with approximately 1 inch of manganese dioxide, MnO_2, in the center or at the outlet end of the tower.

(3) Color change - Indicating DRIERITE is a distinct blue color. When exhausted it turns to a rose red or pink. The zone between the two colors in the column may be a purple color. Regeneration will restore the blue color.

(4) Regeneration - (a) DRIERITE granules should be removed from the column and spread evenly, one granule deep, on a tray. Heat for one hour at about 200°C or 400°F. The desiccant should then be cooled in a tight container before refilling the acrylic unit. Felt filters should also be pre-dried at 100°C for about 30 minutes before assembly. (b) MnO_2 - may be re-used as long as it is dry and not gummy or sticky.

C.5 UV Lamp Replacement

(1) Turn AC power OFF.

(2) Disconnect lamp from transformer with in-line connector. (CAUTION: Power must be OFF before disconnecting lamp from transformer.)

(3) Remove eight 8-32 flat head screws from left side of calibration unit and remove plate.

(4) Loosen Allen set-screw holding UV lamp.

(5) Note position of tip on UV lamp with respect to end wall. Slide lamp out towards rear of unit, removing shield at same time.

(6) Install new lamp with tip at same position as old lamp, installing the shield as the lamp is slid into position.

(7) Tighten Allen set-screw just enough to hold lamp in position, as excessive tightening could damage the lamp insulator.

(8) Opening in the shield should be in position for maximum light through aperture.

(9) Install left side plate and connect in-line power connector.

(10) Turn on AC power.

(11) Calibrate output against known ozone concentration, or use standard KI technique.

C.6 Timer Adjustment

(1) Each timing cam is mounted on the main shaft by means of a heavy duty friction unit which allows for easy finger adjustment of the timing sequence.

(2) The cams may be set for "on-time" of from 2% to 98% of the total overall time cycle.

(3) The cam opening or "on-time" may be adjusted by loosening the cam screw and turning the movable cam to the required degree of opening and then re-tightening the screw.

(4) See Fig. 40 for identification of components.

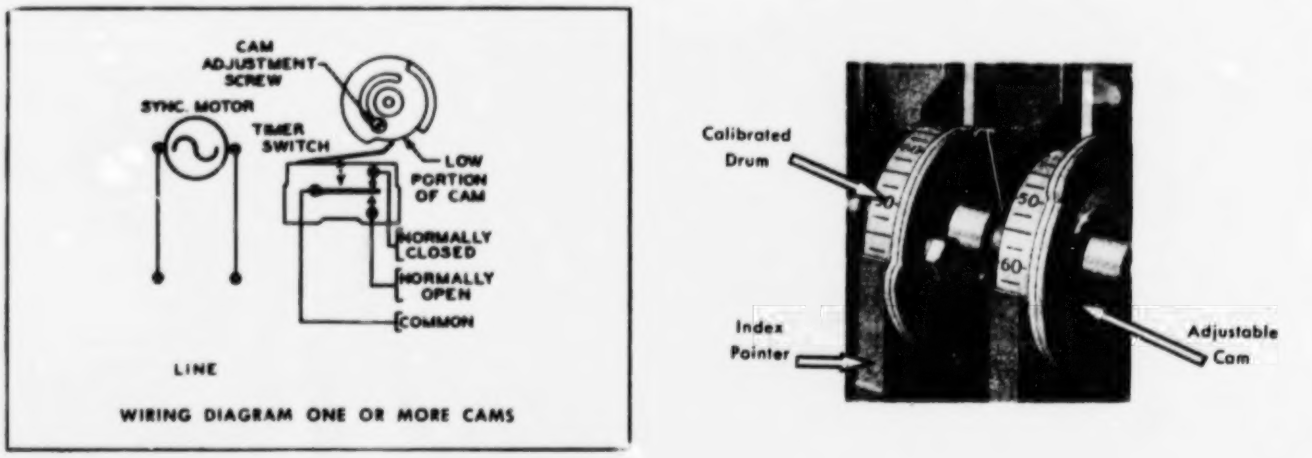

CAM ADJUSTMENT SCREW
SYNC. MOTOR
TIMER SWITCH
LOW PORTION OF CAM
NORMALLY CLOSED
NORMALLY OPEN
COMMON
LINE
WIRING DIAGRAM ONE OR MORE CAMS
Calibrated Drum
50
50
60
Index Pointer
Adjustable Cam

FIGURE 40 . TIMER ADJUSTMENT

C.7 Amplifier Calibration

It is not necessary to remove the amplifier from the unit for this calibration. Simply disconnect the input and attach a voltmeter to the output.

Equipment needed - 10 mV and 10 V source
- Voltmeter - HP-425, or equivalent
- Oscilloscope - Tektronix 547, or equivalent.

All adjustments are located on top of the unit and labeled.

(1) Turn the unit on and allow 30 min for amplifier to stabilize. Leave the input disconnected. Then, turn the sensitivity to 10^{-9}, F.S. output to X1 and time constant to NORM. Adjust R1 for zero output.

(2) Turn the sensitivity control alternately between 10^{-5} and 10^{-9} while adjusting R1 for a minimum change in output between switch settings.

(3) Set the sensitivity control at 10^{-5} and adjust R2 for zero output.

(4) With the input still disconnected, connect an oscilloscope to the output. Set the sensitivity switch at log. Adjust R5 until the output waveform is symmetrical (note there will be a dc offset).

(5) Apply 10 mV to input and adjust R3 for zero output.

(6) Apply 10 V to input and adjust R4 for 1 V output.

(7) Repeat 5 and 6 until change at either setting is minimal.

Amplifier Disassembly - To remove the amplifier from the unit, remove the three knobs and three screws from the front panel. Next disconnect the three BNC connectors from the top of the amplifier and unplug the power cord. The back of the amplifier can now be raised and the unit pulled out over the timing chassis.

C.8 Glass Plumbing Disassembly and Reassembly

Reference points for the assembly or disassembly procedure are shown in Fig. 41. Usual safety precautions for handling glass should be observed during disassembly and reassembly.

(1) DISASSEMBLY:

(a) Loosen fittings at 1 , 2 and 3 and remove the teflon tee with the two glass elbows.

(b) Loosen 1/4 inch fitting at 4 and slide quartz tube toward back of instrument being careful not to put excessive strain on glass fittings.

(c) Loosen fitting at 5 and remove glass elbow.

(d) Loosen fittings at 6 and 7 and remove 1/4 inch copper tubing section.

(e) Loosen fitting at 8 and set screw at 9 and rotate glass coil upward to clear chassis and gently remove from detector assembly.

(2) REASSEMBLY:

Reverse steps 1 through 5 of disassembly, being careful to tighten each fitting as reassembly progresses.

C.9 Calibration Range Change

(1) Turn AC power off.

(2) Disconnect safety chain from rear of chassis and pull chassis forward until calibration unit is completely exposed.

(3) Remove eight 3-32 flat head screws from right side of calibration unit and remove plate.

(4) See Fig. 42 for following steps:

a. To adjust for lower calibration range, set micrometer at 10, loosen the two 4-40 retaining screws and rotate aperture cover counter-clockwise until minimum aperture opening is obtained.

b. To adjust for higher calibration range, set micrometer at 0, loosen the two 4-40 retaining screws and rotate aperture cover clockwise until maximum aperture opening is obtained.

(5) Tighten the aperture cover retaining screws and install side plate.

(6) Calibrate output against known ozone concentration, or use standard KI technique.

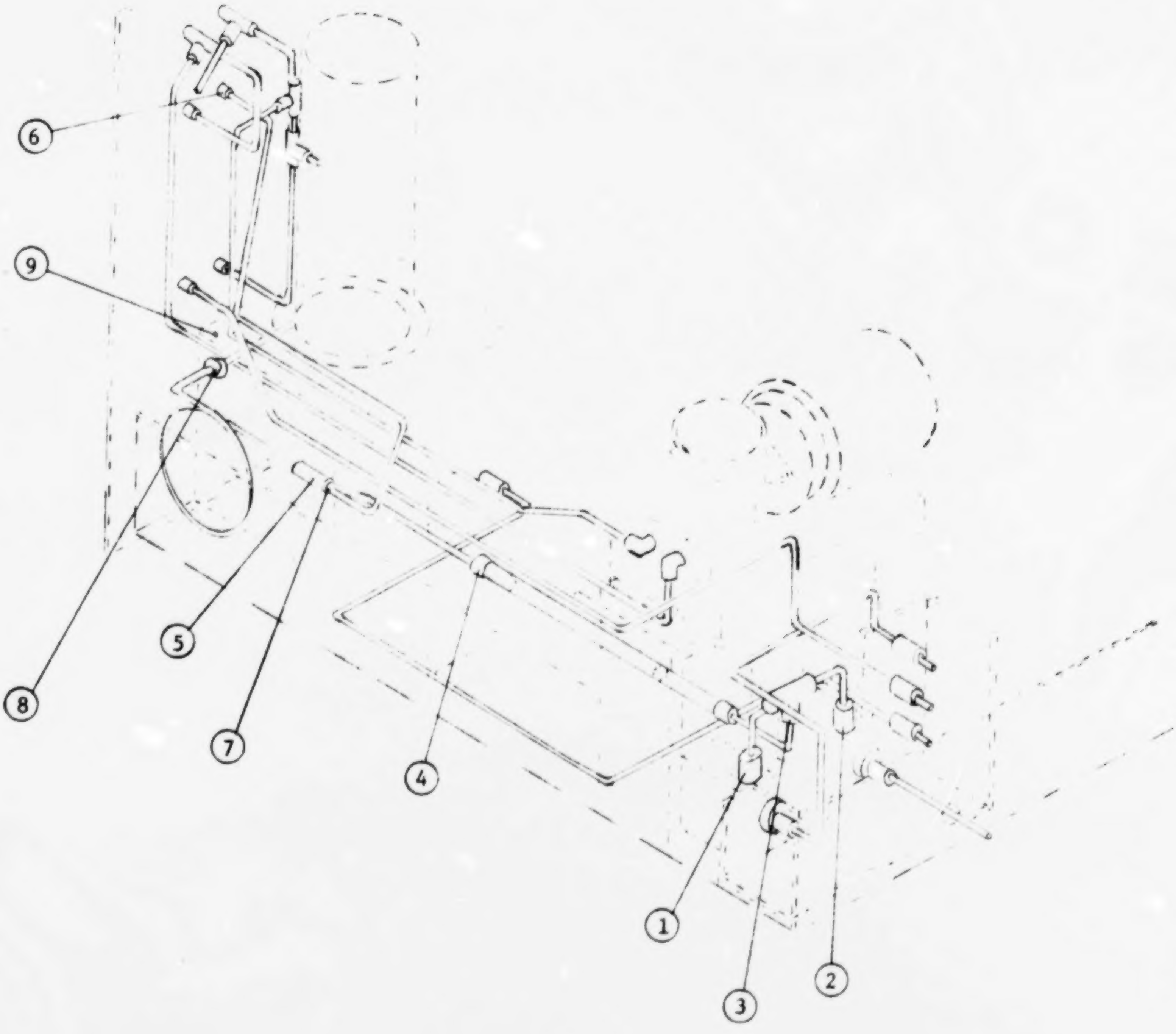
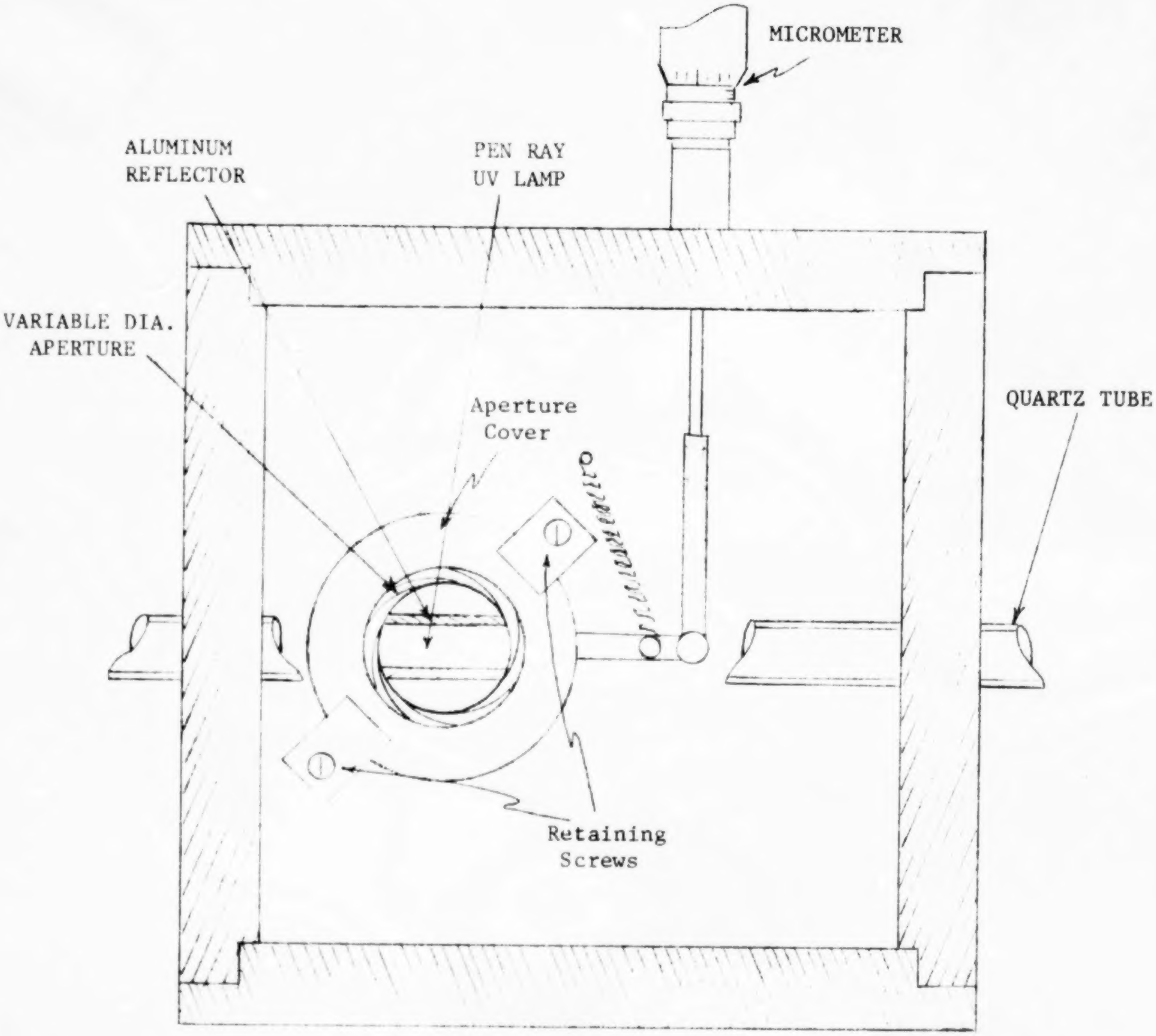


FIGURE 41. DISASSEMBLY AND REASSEMBLY GUIDE


MICROMETER
ALUMINUM REFLECTOR
PEN RAY UV LAMP
VARIABLE DIA. APERTURE
Aperture Cover
QUARTZ TUBE
Retaining Screws

Aperture Adjustment Range

Small: .047" to 0.5" dia.

Large: .5" to .984" dia.

FIGURE 42. CALIBRATION UNIT (side view)

C.10 Replacement of PM Tube

(1) Turn off AC power.

(2) Remove screws from front panel and slide the chassis out until it stops.

(3) Disconnect the HV power supply and signal cables from the top of the PM tube housing.

> CAUTION - When handling PM tubes, avoid exposing the tube to light. This will insure a normal dark current level for the tube. If exposed, allow 24-48 hours for return to normal level.

(4) Remove three 8-32 screws from the PM housing flange and lift the complete housing assembly off the detector unit.

(5) Remove three 6-32 screws from the top of the housing (evenly spread on outside rim) and remove the outer housing.

(6) Remove the Mu-metal shield from the PM tube and then unplug the PM tube.

(7) Install the new tube, reversing the above procedure, being careful not to dislodge the metal grounding braid near the end of the Mu-metal shield nearest the cathode at the PM tube.

NOTE: Light leaks will show up as excessive dark current. Care should be exercised in assemblying the housing.
(a) It may be necessary in some case to use black tape to seal the joints of the housing around the BNC plug end.
(b) An O-ring in the mounting flange of the tube provides an adequate light-tight seal for the open end of the housing.
(c) A check should be made around the PM tube shutter to determine the susceptibility to light leakage.

APPENDIX D

PARTS LIST

A parts list for each of the major sub-assemblies is given in this appendix. The non-standard parts are indicated by an RTI drawing number. All other components are identified by manufacture and manufacturers' part number. Most of the parts listed are self-explanatory. In other sub-assemblies, such as the plumbing assembly, and amplifier unit the specific parts are identified in the respective illustrations.

The high voltage power supply (Power Design, Model 2K-10) and the 12 Vdc supply (Deltron Model C12-2.8) are not included since they are fully described by their respective instruction manuals.

D.1 Detector Assembly

Part No.	Description	Manufacturer	Mfg. Part No.
001	Housing	RTI	Dwg. No. 001
010	PMT Housing	Pacific Photometric	62 (modified length)
020	Photomultiplier	EMI	9558C
030	High Voltage Power Supply	Power Designs Inc.	2K-10
040	Quartz Window (2½ in. diam. x 1/16 in. thick)	Thermal American Fuzed Quartz Company	Vitreosil
050	Jack	Precision Scientific Co.	Little Jack

D.2 Calibration Assembly

Part No.	Description	Manufacturer	Mfg. Part No.
100	Housing	RTI	Dwg. No. 100
120	UV Lamp	Pen-Ray	11SC-1B
130	Lamp Power Supply	Pen-Ray	SCT-3
140	Auto-transformer	Staco	121
141	Knob	Raytheon	70-4-26
150	Milliammeter	Triplett	430
160	Shutter Solenoid	Ledex	H-1079-032
170	Iris Diaphragm	Edmund Scientific	681
180	Micrometer Control	Starrett	440-3RL
190	Quartz tube (standard normal wall 10.2mm o.d. x 8" L)	Thermal-American Fuzed Quartz Company	Spectrosil

D.3 Plumbing Assembly

Part No.	Description	Manufacturer	Mfg. Part No.
1	Bulkhead Adapter	Swagelok	400-A1-4
2	Male Elbow	Swagelok	400-2-2
3	All Tube Tie	Swagelok	40-3
4	Valve, fine metering	Nupro	B-4MA
5	Valve, fine metering	Nupro	B-4M
6	Male Connector	Swagelok	400-1-4
7	Tie connector, teflon	Chemplast	T-T0404-F
8	Reducing Union	Chemplast	T-S0604-F
9	Solenoid Valve	Valcor Engineering	51C70HT34-6A
10	Flow Meter	Brooks Instrument Division	1350-00-BZEAC
11	Drying Tower	W.A. Hammond Drierite Co.	2 5/8" O.D. x 11 3/8"
12	Pump	Neptune Products, Inc.	4K

D.4 Timing Control

Part No.	Description	Manufacturer	Mfg. Part No.
900	Chassis	Bud Radio	AC-403
T1	4 minute timer	Industrial Timer Corp.	MC-5/B12
T2	6 hour timer	Industrial Timer Corp.	CM-10/A12
T3	12 Hour Timer	Industrial Timer Corp.	CM-10/A24
S901	Mode Switch	Switchcraft	37061/H83P/83P
K1	Shutter Meter	Potter & Brumfield	KA11DG
K2	Valve Relay	Potter & Brumfield	KA11DG
B1	"On" Lamps (Mode Switch)	GE	330
PWR1	+ 12V DC Power Supply	Deltron	C12-2.8

D.5 Amplifier Assembly

Part No.	Description	Manufacturer	Mfg. Part No.
500	Chassis	RTI	Dwg. No. 500
R1	100K Potentiometer	Helipot	76PR 100K
R2	50K "	Helipot	76PR50K
R3	20K "	Helipot	76PR20K
R4	2K "	Helipot	76PR1K
R5 & 6	[IN OEI 2245 LOG AMP]		
R7	10K Potentiometer	Bourns	3600S
R8	10K "	Bourns	3007P
R9	9 meg 1% Carbon	IRC	
R10	900K 1% Metal Film	IRC	
R11	100K " " "	IRC	
R12	1K " " "	IRC	
R13	99K " " "	IRC	
R14	9K " " "	IRC	
R15	2.94K " " "	IRC	
R16	1K " " "	IRC	
R17 & 18	20K " " "	IRC	
R19	4020 ohms " "	IRC	
R20 & 21	[Trim resistors furnished with AD 183K amplifiers]		
R22	2K 1% Metal Film		
R23 & 24	1K " " "		
R25 & 26	200K " " "		
R27	1000 Meg ohm,	Victoreen	
R28	10K Trimpot	Beckman	76PR10K
R29	10K Potentiometer 10T	Bourns	3600S
R27	100 ohms 1% Metal Film	IRC	
R28 & 29	1 meg " " " "	"	
R30	15K " " " "	"	
R31	13K " " " "	"	

Amplifier Assembly (Continued)

Part No.	Description	Manufacturer	Mfg. Part No.
R32	1K Potentiometer	Helipot	76PR1K
C1	1.0 µf	CDE	225P1059R75
C2	1.0 µf	Sprague	113D-106C701500
C3	40 µf	Sprague	113D-406C7015C0
S501	Sensitivity Switch	Centralab	P-505/(3)PS-21
S502	Full Scale Output Switch	Centralab	P-503/(1)PS-21
S503	Time Constant Switch	Centralab	P-503/(1)PS-21
A1	Operational Amp.	Analog Devices	311K
A2 & A3	Operational Amp.	Analog Devices	183K
A4	Logarithmic Amp.	OEI	2245A
M1	Output meter	Triplett	1150
	Knobs	Raytheon	50-4-1G

D.6 Chassis and Cabinet

Part No.	Description	Manufacturer	Mfg. Part No.
701	Chassis	RTI	Dwg. No. 700
800	Cabinet	Optima	E-171920H
801	Front Panel	Optima	P-14
802	Rear Panel	Optima	P-7
803	Rear Door	Optima	D-10
804	Handles	Optima	H-14
805	Chassis Slides	Chassis-Trak	C-230-S-18
806	Fan	Rotron Mfg. Co.	Muffin Fan
401	Solenoid Valve Bracket	RTI	Dwg. No. 400
301	Clean-up Tower Bracket	RTI	Dwg. No. 300
200	Pump Mounting Bracket	RTI	Dwg. No. 200

D.7 Interlock Circuit

Part No.	Description	Manufacturer	Mfg. Part No.
TR1	Transformer (12.6 VAC)	Chicago-Stancor	P8130
S101	Full Open Switch	Robertshaw	1MD1-1A
S102	Full Closed Switch	Robertshaw	1MD1-1A
S103	Door Open Switch	Robertshaw	1MD1-1A
BZ1	Buzzer	Potter & Brumfield	12VDC
B101	Full Open Lamp	Dialco/GE	182-8430/327
B102	Full Closed Lamp	Dialco/GE	182-8430/327

D.8 AC Power

Part No.	Description	Manufacturer	Mfg. Part No
S1	Power Switch	Arrow Hart	81024GB
F1	Fuse	Littlefuse	3AG-10AMP
PS1	Power Strip	CBC Electronics	MO-G-D